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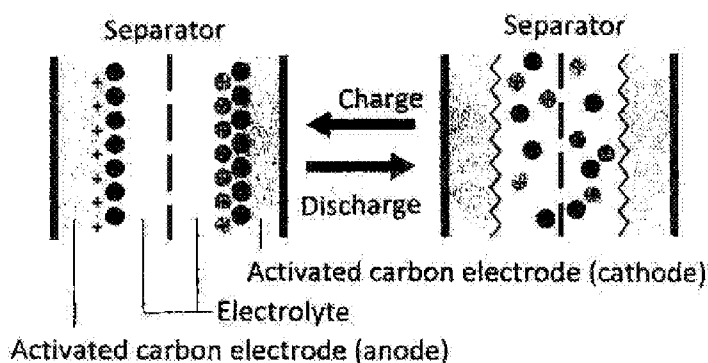


Fig. 1A

(57) **Abstract:** Capacitors containing novel electrodes and electrolytes are described. One electrode composition comprises an oxide of Mn and Fe in a Mn:Fe molar ratio of 3:1 to 5:1. Another electrode composition comprises an oxide comprising Ni, Co, and Fe; wherein the Ni and Co are present in a Ni/Co molar ratio in the range of 0.5 to 2 and a Fe and Ni are present in a Ni/Fe molar ratio in the range of 1.0 to 10. The resulting capacitors can be characterized by superior properties. Methods of forming the electrodes from gels are also described. An electrolyte comprising a Li salt in a carbonate solution, wherein the carbonate solution comprises 10-30% ethylene carbonate and 70-90% propylene carbonate is also described.

Supercapacitor Materials and Devices

Related Application

This application claims priority to US provisional patent application serial no. 61/165,491, filed 31 March 2009.

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Background

Conventionally, electrical power has usually been stored in batteries. Another device for storing energy is a capacitor, and more recently the so-called supercapacitor. Very substantial efforts have been made to develop improved capacitors for storing electrical energy.

10 The requirement for capacitance is the ability to separate charge at a specified potential. The prototypical capacitor consists of two metal plates, with a potential difference between the plates. In the charged state, one plate will have a net positive charge, the other a net negative charge. The capacitance can be determined from the area of the plates and the separation between the plates. Placing a solid dielectric material between the plates increases the
15 capacitance, as the same potential difference between the plates leads to larger net charge on each plate.

Recent developments in capacitor technology have led to replacement of the metal plates with high surface area conductive materials, such as carbon, and replacement of the solid dielectric with a liquid electrolyte. In case of carbon electrodes, the capacitance arises from the
20 double layer mechanism, where the ions in the electrolyte move adjacent to the electrode surface. In this case, the capacitance increases due to two factors, the increase in the area of the electrode due to the porosity, and the decrease in the charge separation distance.

The recent developments in synthesis of high surface area materials have also led to the development of capacitors based on a second mechanism, the so-called faradaic capacitors. The
25 faradaic capacitors are composed of a solid state electrode with a liquid electrolyte. The operation principle of these capacitors is based on reversible reactions at the interface at certain potential. There are different characteristics of the second type of capacitors; the charge transfer reaction occurs at the interface of the outer porous layer, the substrate (current collector) is different material than the external layer. The ions are integrated in the structure of the high
30 surface area material (commonly an oxide or nitride) by reacting either by substitution or by

integration of the ion within the structure of the material. To cite just one example, see Piao et al. "Intercalation of Lithium Ions into Graphite Electrodes studied by AC Impedance measurements," J. Electrochem Soc. 146, 2794-2798 (1999). The stability will depend on the reversibility of this reaction (or process). If the reduction or oxidation process consumes more species than the reversible reaction, or if there is another species formed at the surface, the reversibility is modified.

Recently, a third type of capacitor, the "hybrid" capacitor has also been reported. In this capacitor, both the double-layer and the faradaic mechanism are used, to provide enhanced capacitance, and to take advantage of operational advantages of each mechanism.

The solid state electrode can be composed of a nanoporous transition metal compound placed on a high surface area conductive medium, such as carbon black, or carbon nanotube (CNT) films, combined with a binder to ensure physical integrity. If the ions move into the transition metal compound, the capacitance mechanism is faradaic, or possibly hybrid, while if the ions do not enter the transition metal compound the mechanism is purely double layer.

There are numerous reports in the prior art describing methods of forming electrodes from composites of carbon and metal oxides or mixed metal oxides. For example, Kim et al. in "Synthesis and Characterization of MnO_2 -Based Mixed Oxides as Supercapacitors," J. Electrochem. Soc. 150 D56-D62 (2003) describe the preparation of Mn/Pb and Mn/Ni mixed oxides by reduction of KMnO_4 with Pb and Ni salts. Jayalakshmi et al. in "Hydrothermal synthesis of SnO_2 - V_2O_5 mixed oxide and electrochemical screening of carbon nano-tubes (CNT), V_2O_5 , V_2O_5 -CNT, and SnO_2 - V_2O_5 -CNT electrodes for supercapacitor applications" J. Power Sources 166 (2007) 578-583 report the preparation of mixed metal oxides for electrodes by hydrothermal synthesis. Walker et al. in "Sol-gel synthesis of hydrous ruthenium oxide nanonetworks from 1,2-epoxides," J. Solid State Chemistry 180 (2007) 2290-2297 reported the synthesis of a RuO_2 xerogel formed by the addition of propylene oxide to ruthenium chloride in ethanol. A report on the use of propylene oxide to form a mixed metal oxide is by Cui et al., "A sol-gel route using propylene oxide as a gelation agent to synthesize spherical NiAl_2O_4 nanoparticles" J. Non-Cryst Solids 351 (2005) 2102-2106. Kuan-Xin et al. in "Electrodeposition of Nickel and Cobalt Mixed Oxide/Carbon Nanotube Thin Films and Their Charge Storage Properties," J. Electrochem. Soc., 153, A1568-A1574 (2006) reported a method of electrochemically depositing a mixed metal oxide on a film of carbon nanotubes.

A liquid electrolyte is either aqueous, with a high concentration of acid, base, or salt, or non-aqueous with a salt dissolved in an organic or inorganic solvent. There are a wide variety of solvents and salts are available for such use, offering specific advantages depending on the application being considered (e.g., low temperature vs. high temperature). Ionic liquids based on the imidazolium cation have recently received attention as nonaqueous electrolytes in various electrochemical devices (Koch et al., J. Electrochem. Soc. 143:155, 1996). These electrolytes have significant advantages compared to the numerous quaternary onium salts that have been previously investigated for use in carbon double-layer capacitor.

Electrochemical capacitors based on nonaqueous electrolytes offer greater electrochemical stability (up to 4 V) compared to aqueous systems (limited to approximately 1V), thereby providing greater energy storage ($E=1/2CV^2$). However, due to the lower conductivity of nonaqueous electrolytes compared to aqueous systems, lower power capabilities are observed. In addition, with the porous materials used in electrochemical capacitors, the high viscosity typically associated with the high dielectric constant solvents used in nonaqueous electrolytes is detrimental to conductivity in porous electrodes. Furthermore, the lower ion concentrations typically obtained with nonaqueous electrolytes result in increased electrolyte volume requirements for packaged devices.

U.S. Patent No. 6,339,528 describes a capacitor made by in-situ formation of MnO_2 on carbon black and various ratios of MnO_2 , carbon black and PTFE binder. In the data presented, there appear to be no correlations between the volume of MnO_2 with the volume of carbon black or the volume of PTFE. There are no correlations with any of the variables with the specific capacitance results.

Despite extensive research and development, there remains a need for improved capacitors for the storage of energy.

Summary of the Invention

In a first aspect, the invention provides a capacitor comprising: an electrode, and wherein the electrode comprises: a metal oxide comprising Mn and Fe in a molar ratio of 3:1 to 5:1. In some preferred embodiments, the electrode comprises Mn and Fe in a molar ratio of 3.5:1 to 4.5:1, and in some embodiments, a molar ratio of 4:1. In some embodiments, the transition metals in the metal oxide consist essentially of Mn and Fe. In some embodiments, the electrode

comprises 5 weight % or less of binder. In some embodiments, the electrode comprises carbon, for example in the form of carbon black and/or carbon nanotubes. As shown in the examples, electrode performance is affected by the size of the electrode; thus, in some preferred
embodiments, the electrode has a mass in the range of 0.1 to 2 mg. In some preferred
5 embodiments, the electrode comprises 40 to 80 weight% metal oxide nanoparticles and 15 to 60 weight% carbon. In some preferred embodiments, the electrode comprises at least 5 weight% carbon nanotubes. In some preferred embodiments, the metal oxide further comprises Ni, Co, or a combination of Ni and Co.

Any of the inventive capacitors (or electrode in the capacitor) may also be characterized
10 by any of its properties, for example, wherein the metal oxide is characterizable by an absorption band in the infrared region between 1000 and 1100 cm^{-1} ; or In general, the inventive capacitors (or electrode in the capacitor) can be characterized by any of the properties shown in the examples, either based on a selected range of properties shown in the figures, or using a selected demonstrated property to form the basis for a minimum or maximum level of a property. For
15 example, in some preferred embodiments the electrode comprises a specific capacitance of at least 500 F/g if measured at 1 mV/s in 1M KOH aqueous electrolyte. The conditions described in the examples may be used to define the conditions under which a selected property is to be measured.

The capacitor may also be characterizable by an x-ray diffraction spectrum in which the
20 peaks due to a crystalline hydroxide compound are larger than the peaks due to crystalline oxide compounds.

In another aspect, the invention provides a capacitor comprising: an electrode, and wherein the electrode comprises: a metal oxide comprising Ni, Co, and Fe; wherein the Ni and Co are present in a Ni/Co molar ratio in the range of 0.5 to 2 and Fe and Ni are present in a Ni/Fe
25 molar ratio in the range of 1.0 to 10. In some preferred embodiments, the electrode further comprises Mn.

The invention further provides a capacitor comprising: a first electrode as described in any of the aspects described herein; an electrolyte; a second electrode; and a circuit that can form an electrical pathway between the first electrode and the second electrode. In some preferred
30 embodiments, the electrolyte is a nonaqueous liquid. In some preferred embodiments, the first and second electrodes have substantially the same composition.

In another aspect, the invention provides a capacitor, comprising: two electrodes; an electrolyte between the electrodes; wherein the electrolyte comprises a Li salt in a carbonate solution, wherein the carbonate solution comprises 10-30% ethylene carbonate and 70-90% propylene carbonate. In some preferred embodiments, the carbonate solution comprises 15-25% ethylene carbonate and 75-85% propylene carbonate. In some preferred embodiments, the Li salt comprises LiBF_4 , LiPF_6 or a combination of LiBF_4 and LiPF_6 . In some preferred embodiments, at least one of the electrodes comprises metal oxide nanoparticles in a carbon matrix. The capacitor preferably comprises a porous polymeric separator disposed between the electrodes. In some preferred embodiments, the metal oxide comprises vanadium oxide, iron oxide, iron-manganese oxide, iron-nickel oxide, iron-copper oxide, cobalt-manganese oxide, manganese-titanium oxide, BaFeO_4 , or combinations thereof.

In another aspect, the invention provides a method of making an electrode, comprising: forming a composition comprising Mn and Fe in a molar ratio of 3.5:1 to 4.5:1; reacting the composition to form a gel comprising Mn and Fe in a molar ratio of 3.5:1 to 4.5:1; drying the gel to obtain a powder comprising Mn and Fe in a molar ratio of 3.5:1 to 4.5:1; and compacting the powder to form an electrode. In some embodiments, gel is dried in the presence of supercritical CO_2 to form an aerogel. In some embodiments, the step of reacting comprises reaction with an epoxide. In some preferred embodiments, the temperature of the process never exceeds 200 °C, so that the powder comprising Mn and Fe remains substantially amorphous.

In a further aspect, the invention provides a method of making a capacitor comprising: providing two electrodes; providing an electrolyte between the electrodes; wherein the electrolyte comprises a Li salt in a carbonate solution, wherein the carbonate solution comprises 10-30% ethylene carbonate and 70-90% propylene carbonate.

The invention also provides methods of storing energy comprising: applying a potential to any of the capacitors described herein, removing the potential; and wherein, after the potential is removed, an electrical potential persists between the electrodes.

In another aspect, the invention provides a method of making a capacitor, comprising: providing a carbon electrode in a first Li-containing solution; intercalating Li into the electrode to form a Li-intercalated electrode; removing the electrode from the first Li-containing solution; and placing the Li-intercalated electrode into a second Li-containing solution. The second Li-

containing solution is typically part of a supercapacitor that comprises the other components of a supercapacitor.

In a further aspect, the invention provides a method of making an electrode, comprising: forming a solution comprising carbon particles and a dissolved metal compound; reacting the metal compound to form a gel; converting the gel into metal oxide nanoparticles; combining the metal oxide nanoparticles with a binder; and compacting the metal oxide nanoparticles and binder into an electrode. In some embodiments, the solution comprises Mn and Fe in a molar ratio of 3:1 to 5:1. In some embodiments, the solution is gelled by the addition of an epoxide. In some embodiments, the solution comprises Mn, Co and Fe.

The invention also includes electrodes formed by any of the methods described herein, and/or capacitors comprising any of the electrodes. In preferred embodiments, the capacitors and/or electrodes can be described with reference to the properties described in the examples. For example, in some preferred embodiments, the capacitors possess a stability such that they exhibit substantially no change in capacitance after 100 cycles. The invention also includes devices comprising the capacitors; for example a solar energy system comprising a photovoltaic cell connected to the capacitor. The invention also includes methods of storing energy using any of the capacitors described herein.

The capacitors can be characterized by their properties including specific capacitance, energy density, stability, high voltage and and storage capabilities.

The invention can be described with the word “comprising” meaning “including,” and when “comprising” is used, the invention also includes narrower, alternative embodiments, in which “comprising” is replaced by the terms “consisting essentially of” or “consisting of”.

Glossary

In reference to the carbonate solution, “%” refers to % by liquid volume measured at 40 °C. For example, a solution made by mixing 4 ml ethylene carbonate and 6 ml propylene carbonate (at 40 °C) would be 40% ethylene carbonate and 60% propylene carbonate. In a solution, the amount of each component could be determined by spectroscopy or quantitative gas chromatography and then calculating the volume of each pure component at 40 °C (the volume percent would then be the volume of one component divided by the sum of each component’s volume).

An "Electrode" is a well-known term that refers to a conductive component of a capacitor that contacts the electrolyte.

"Electrolyte" is a composition comprising one or more ionic species and a medium through which ions can move. In preferred embodiments, the electrolyte comprises a non-
5 aqueous liquid, preferably containing less than 100 ppm water, and containing a dissolved salt.

"Intercalating" refers to the reversible inclusion of lithium into an electrode.

"Ionic species" means an ion, or a compound that forms an ion as part of an electrolyte (i.e., forms an ion under conditions in the capacitor; for example, a carboxylic acid can be converted to an ion in the appropriate solvent).

10 "Lithium salts" are well known materials for use in electrolytes and include compounds such as $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiBF_4 or LiPF_6 .

Metal oxides comprise transition metal atoms connected by bridging oxygen atoms. Metal oxide particles may also contain other atoms such as B, N, C, Al, Zn, etc. Metal oxides will often also comprise hydroxyl groups which diminish in concentration with heating. In some
15 preferred embodiments, metal oxides consist essentially of transition metals (or metal), oxygen, and, optionally, H in the form of hydroxides..

"Mixed metal oxides" are metal oxides comprising at least two different transition metals.

20 "Nanoparticles" are particles in the size range of 1 to 1000 nm, preferably in the range of 1 to 100 nm.

A "separator" is a porous sheet placed between the positive and negative electrodes in an electrolyte. Its function is to prevent physical contact of the positive and negative electrodes while serving as an electrolyte reservoir to enable free ionic transport. Typically, the separator is a polymeric or ceramic microporous membrane or a nonwoven cloth. The microporous
25 membranes are preferably 25 μm or less in thickness and have an average pore size of 1 μm or less (volume average).

"Transition metals" have the standard IUPAC definition of "an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell."

30 For purposes of the present invention, a capacitor (or supercapacitor) that includes a separator has the general structure illustrated in Fig. 1A. Note that the electrodes may include any of the electrodes described herein and may not be formed as a single homogeneous mass as

depicted in the figure. Also note that the energy in this depiction is stored through a double layer mechanism. The capacitors of this invention may also incorporate energy storage through the intercalation of charge into the electrode materials. Note further that, although a separator is typically desirable for structural stability, in some highly rigid structures is possible to omit the separator. The two electrodes are also connected, or connectable, to an external circuit that is the energy source during charging and is where useful work can be done during discharge of the capacitor.

Brief Description of the Drawings

- Fig. 1A is a schematic illustration of a double layer capacitor.
Fig. 1B illustrates a half cell design for measuring electrochemical properties.
Fig. 2 illustrates specific capacitance of vanadium oxide as a function of voltage scan rate.
Fig. 3 illustrates scan rate dependence of the specific capacitance of vanadium oxide electrodes.
Fig. 4 illustrates the dependence of specific capacitance of vanadium oxide electrodes as a function of composition.
Fig. 5 illustrates specific capacitance of vanadium oxide electrodes for various carbon media.
Fig. 6 shows the specific capacitance as a function of electrode mass for various oxides.
Fig. 7 shows the total capacitance as a function of electrode mass for various oxides.
Fig. 8 shows the specific capacitance as a function of electrode mass for various oxides, obtained at a fast scan rate.
Fig. 9 shows the specific capacitance as a function of electrode mass for various ratios of Fe:Mn obtained at 10 mV/s in 1M KOH aqueous electrolyte.
Fig. 10 shows the specific capacitance as a function of electrode mass for various ratios of Fe:Mn obtained at 1 mV/s in 1M KOH aqueous electrolyte.
Fig. 11 shows the specific capacitance as a function of electrode mass for various oxides, obtained at 10 mV/s.
Figs. 12-15 show the specific capacitance as a function of electrode mass for various oxides, obtained at 1 mV/s.
Fig. 16 shows a log plot of specific capacitance as a function of voltage scan rate.
Fig. 17 is a plot of specific capacitance as a function of voltage scan rate for FeMn₄ oxide in 1M KOH aqueous electrolyte.

Fig. 18 is a plot of specific capacitance as a function electrode mass for FeMn_4 oxide in 1M KOH aqueous electrolyte measured at three different voltage scan rates.

Fig. 19 is a plot of specific capacitance as a function electrode mass for FeMn_4 oxide with varying amounts of carbon, obtained at 1 mV/s in 1M KOH aqueous electrolyte.

5 Fig. 20 is a plot of specific capacitance as a function electrode mass for FeMn_4 oxide with different binders, obtained at 1 mV/s in 1M KOH aqueous electrolyte.

Fig. 21 is a plot of specific capacitance as a function electrode mass for FeMn_4 oxide, obtained at 1 mV/s in various aqueous electrolytes.

10 Fig. 22 a plot of specific capacitance as a function electrode mass for $\text{FeMn}_4\text{Ni}_{0.5}\text{Co}_{0.5}$ oxide, obtained at 1 mV/s.

Fig. 23 illustrates scan rate dependence for various non-aqueous electrolytes.

Fig. 24 shows specific capacitance of FeMn_4 oxide in a 50/50 volume mixture of ethylene carbonate and propylene carbonate (EC/PC).

Fig. 25 shows specific capacitance of FeMn_4 oxide in 20/80 EC/PC.

15 Fig. 26 shows specific capacitance of FeMn , FeMn_4 , and FeMn_8 oxides in 80/20 EC/PC.

Fig. 27 shows the response of FeMn_4 oxide in 50/50 EC/PC with 0.1 M LiPF_6 .

Fig. 28 shows the capacitance over numerous cycles of FeMn_4 oxide in 50/50 EC/PC with 0.1 M LiPF_6 .

20 Fig. 29 shows the capacitance of FeMn_4 oxide in 50/50 EC/PC with 0.1 M LiPF_6 in a full-cell configuration.

Fig. 30 shows an x-ray diffraction (XRD) plot of FeMn_4 oxide dried at 50°C.

Fig. 31 shows an x-ray diffraction (XRD) plot of FeMn_4 oxide dried at 100°C.

Fig. 32 shows infrared (IR) spectra of FeMn_4 oxide after calcination at 5 different temperatures.

25 ***Detailed Description of the Invention***

Solid state electrodes for supercapacitors can be formed, for example, from oxides, hydroxides, sulfides, phosphates (or combinations thereof) with transition metals such as Manganese, Iron, Cobalt, Nickel (or combinations thereof) with CNT and/or carbon black in different ratios.

30 A preferred electrode of the present invention comprises oxides of Fe and Mn having a Mn and Fe in a molar ratio of 3:1 to 5:1, more preferably a molar ratio of 3.5 to 4.5, and in some

embodiments, a molar ratio of 4:1. Additional transition metal elements may also be present in the metal oxide; for example, Ni, Co, or a combination of Ni and Co.

In an alternative embodiment, an electrode comprises a metal oxide comprising Ni, Co, and Fe; wherein the Ni and Co are present in a Ni/Co molar ratio in the range of 0.5 to 2 and Fe and Ni are present in a Ni/Fe molar ratio in the range of 1.0 to 10. The metal oxide can contain additional elements. In some preferred embodiments, the electrode further comprises Mn.

In addition to the oxide in particle form, the electrodes typically contain carbon particles as the conductive phase. Carbon materials are well known, and a variety of carbon particles may be used in the electrodes. In some preferred embodiments, the carbon material comprises carbon nanotubes (CNTs), in some embodiments at least 5 weight% CNTs as a percent of the mass of the electrode. In some preferred embodiments, the electrode comprises 40 to 80 weight% metal oxide particles (preferably nanoparticles) and 15 to 60 weight% carbon.

Typically, it is necessary to add a binder in order to form the electrode in a desired shape. Binders for making electrodes are known. Nonlimiting examples of binders include: PTFE, Nafion, Epoxy resin, Polyvinylidene fluoride (PVDF), Polyvinylidene fluoride-hexafluoropropylene (PVDF-HEP), ZrO_2 , and TiO_2 . Since binders reduce conductivity, when binders are present, it is preferred to keep them at a level of 5 mass% or less of the electrode's mass.

A supercapacitor also includes an aqueous or nonaqueous electrolyte. Examples of nonaqueous solvents for electrolytes include propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), 1,2-dimethoxyethane (DME) and 1,2-diethoxyethane (DEE). As is known in the art, electrolytes further comprise a salt. In the present invention, the salts preferably contain Li ions and counter ions such as PF_6^- , BF_4^- . Although the relative amounts of ethylene carbonate and propylene carbonate were not previously known to affect the properties of a capacitor, we have surprisingly discovered that superior results can be obtained with the electrolyte comprises 10-30% ethylene carbonate and 70-90% propylene carbonate. In some preferred embodiments, the carbonate solution comprises 15-25% ethylene carbonate and 75-85% propylene carbonate. The electrolyte can be used in conjunction with electrodes containing a metal oxide, preferably mixed with carbon. In some preferred embodiments, the metal oxide comprises vanadium oxide, iron oxide, iron-manganese oxide,

iron-nickel oxide, iron-copper oxide, cobalt-manganese oxide, manganese-titanium oxide, BaFeO_4 , or combinations thereof.

The electrodes may be characterized by any of the properties described in the examples. For example, a specific capacitance (or, alternatively, total capacitance) of the same level or
5 greater than that shown in the examples.

The inventive capacitors are especially useful for storing energy from renewable energy sources such as solar, wind, and tidal. In these systems, charge is stored during periods of high energy production, and can be used when little or no energy is being collected. The capacitor may have parallel plates. Alternatively, the capacitor can be in the form; for example, the
10 electrodes and separators can be alternately stacked, wound into a roll, and electrolyte poured in, then sealed to form a supercapacitor energy storage device.

The electrodes can be made using mixed metal oxides that are obtained by the sol-gel method to obtain a xerogel or aerogel which can then be ground into a powder and incorporated into an electrode. It has been discovered that an electrode with superior properties can be
15 obtained when the carbon material is mixed in solution with a metal compound prior to formation of the gel. Epoxides have been found to work well to react with the metal compound(s) to form a gel.

Alternatively, the mixed metal oxides can be made by a hydrolysis method, such as that described in the examples.

The mixed metal oxides are preferably not heated above 250 °C, more preferably not heated above 200 °C, and in some embodiments not heated above 100 °C. Contrary to a prior art report for Fe_2Mn oxide (see Kuo et al., "Electrochemical characterization on MnFe_2O_4 /carbon black composite aqueous supercapacitors," J. Power Sources 162 (2006) 1437-1443), we have surprisingly discovered that heating reduces specific capacitance.

25 *Examples*

Electrochemical Characterization

The fabricated electrodes were characterized to determine their capacitance, voltage window, open circuit potential, and other parameters. Figure 1b shows a half-cell configuration used for measuring the capacitance of the electrodes.

The general sequence of experiments used to characterize the electrodes includes the following steps:

- Open circuit potential with time (1h)
- Electrochemical Impedance Spectroscopy (10 mV amplitude) 10KHz to 0.01Hz
- 5 • Cyclic voltammetry (aqueous solutions 0.7V vs. SCE to -0.7 vs. SCE)
- Analysis of the results (currents, voltage and capacitance)

The values of specific capacitance reported here are measured using cyclic voltammetry.

Although some electrodes have been characterized for 100 voltage cycles or more, the reported capacitance is routinely determined from the second voltage cycle.

Comparison to Literature Capacitance Measurements

Two types of capacitance values will be reported here, the total capacitance and the specific capacitance. The specific capacitance is the total capacitance divided by the mass of the electrode, and so has units of F/g. The specific capacitance is often reported in the literature, as a
 15 measure of how effectively charged is being stored in or adjacent to the electrode. The total capacitance is of the most interest, as a measure of the value of the material for commercial applications.

Care must be exercised when comparing the data of this invention to data reported in the open literature. The common practice in the literature is to report the specific capacitance of
 20 metal oxide electrodes by dividing the measured capacitance by the mass of the metal oxide only. The largest capacitance values that are reported typically occur when the oxide is approximately 10% of the total electrode mass. For example, in 2006 *J. Electrochem. Soc. pp. A1451*, the authors present data for the capacitance of vanadium oxide deposited onto CNT films, when measured at a scan rate of 1mV/sec, as shown in Table 1.

Table 1. Specific capacitance of V₂O₅ on CNT films taken from the literature.

% mass of V ₂ O ₅	Capacitance using Vanadium mass	Capacitance using total electrode mass
8.9 wt%	1230 F/g	109.5 F/g
33.9 wt%	650 F/g	220.4 F/g

51.3 wt%	310 F/g	159 F/g
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From Table 1, we see that the reported best value of 1230 F/g for the vanadium oxide capacitance is actually from the electrode with the lowest total capacitance. In many cases, the conductive component of the electrode will contribute double layer capacitance, which should also be accounted for. In cases where the transition metal compound is only 10% of the electrode mass, the double layer capacitance can be of the same order of magnitude as the faradaic component.

To avoid these complications, all specific capacitance values reported in this document will be based on the total mass of the electrode, including the binder and the conductive component.

Metal Oxide/Hydroxide Synthesis and Characterization

There were two primary approaches used to synthesize the metal nanoparticles, either a hydrolysis process, or a xerogel process. For some materials, both approaches were used. In all cases, the particles are expected to have a high degree of hydroxide nature, as the drying occurs at a temperature below that normally needed to completely convert the hydroxide to oxide. These materials will be referred to generically as oxides throughout the text. In cases where the material is labeled with elements and numbers, such as Fe₁Cu₂, this indicates the oxide was formed at a nominal starting molar ratio of one Fe to two Cu. Representative synthesis methods for the oxides are included below.

Sample Synthetic Methods

Preparation of iron oxide/hydroxide aerogel

4.39 g FeCl₃·6H₂O and 1.17 g water were dissolved in 20 g ethanol. 10 g propylene oxide (PPO) was added quickly into the alcoholic solution under stirring with a gel forming in less than 16 minutes. The formed gel was aged with sealing for several days at room temperature. The solvent (ethanol and water) in the gel was exchanged with acetone at least three times (one day one time). The acetone exchanged gel was finally dried by supercritical CO₂.

Iron-cobalt mixed oxide/hydroxide, iron-manganese mixed oxide/hydroxide and iron-nickel mixed oxide/hydroxide were prepared in a similar fashion, starting from:

- 2.20 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 1.86 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.59 g water were dissolved in 20 g ethanol (iron-cobalt oxide/hydroxide);
- 2.20 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 1.54 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, and 0.59 g water were dissolved in 20 g ethanol (iron-manganese oxide/hydroxide); and
- 5 • 2.20 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 1.85 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.59 g water were dissolved in 20 g ethanol (iron-nickel oxide/hydroxide).

Preparation of vanadium oxide/hydroxide aerogel

10 0.6 g $\text{VO}(\text{OPr})_3$ was dissolved in 8 g isopropanol. The solution was then cooled with ice. 1.8 g water was added to the cold alcoholic solution with stirring. A gel formed within several minutes. The wet gel was aged and treated with acetone before supercritical CO_2 drying as for iron-based gels.

Preparation of vanadium-iron mixed oxide/hydroxide aerogel

15 0.6 g $\text{VO}(\text{OPr})_3$ was dissolved in 5 g ethanol. 0.664 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to the ice-cold alcoholic solution. 1.2 g water was added after FeCl_3 was dissolved, then 2 g propylene oxide was added and a gel formed within 1 minute. The wet gel was aged and treated with acetone before supercritical CO_2 drying as for iron-based gels.

20 *Preparation of vanadium-manganese mixed oxide/hydroxide aerogel*

0.6 g $\text{VO}(\text{OPr})_3$ was dissolved in 8 g ethanol. 0.486 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 1.2 g water were added to the ice-cold alcoholic solution, and a gel was obtained after sitting overnight. The wet gel was aged and treated with acetone before supercritical CO_2 drying as for iron-based gels.

25 *Preparation of Fe-Cu mixed oxide xerogel*

2.20 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 1.39 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and 0.62 g water were dissolved in 20 g ethanol. 10 g propylene oxide (PPO) was added quickly into the alcoholic solution under stirring. A gel was formed within 15 minutes. The formed gel was dried in air for 2 days, dried at 50 °C for 2 days, and dried at 50 °C under vacuum for 1 day.

30

Preparation of Co-Mn oxide xerogel

1.86 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 1.54 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, and 1.50 g water were dissolved in 20 g ethanol. 10 g propylene oxide (PPO) was added quickly into the alcoholic solution under stirring. The solution was left in air until it was dried. The soft precipitate was dried at 50 °C for 2 days, and dried at 50 °C under vacuum for 1 day.

5

Preparation of Mn oxide xerogel

0.145 g fumaric acid was dissolved in 10 g water under heating. When the solution was still warm, 0.59 g KMnO_4 was added under stirring. A gel formed within 2 minutes. The formed gel was soaked in 0.1 M H_2SO_4 twice and then rinsed with ethanol. A black powder was obtained after drying the gel at 50 °C for 2 days, and then 50 °C under vacuum for 1 day.

10

Preparation of Mn-Ti mixed oxide xerogel

3.52 g manganese acetylacetonate, 2.45 g titanium ethoxide (95%), 0.11 g HCl (37%) were dissolved in 9.2 g isopropanol, then 15 ml aqueous ammonia (28%) was added to the above solution under stirring. A gel formed within 5 minutes. The formed gel was dried in air for one day, dried at 50 °C for 2 day, and dried at 50 °C under vacuum for 1 day.

15

Preparation of BaFeO_4

100 ml 2 M KOH solution was cooled by ice bath with bubbling of N_2 . 0.25 g K_2FeO_4 was added to the above solution with stirring. N_2 was continued to bubble through the solution for more than 5 minutes. In another beaker, 0.313 g barium acetate was dissolved in 80 ml water. The solution was cooled with ice and bubbled with N_2 for more than 15 minutes. The solution of K_2FeO_4 was added into barium acetate solution under fast stirring. The precipitates were washed and collected by centrifuge after aged for 15 minutes in the solution. The collected precipitates were dried in oven at ~ 100 °C for overnight, then the dried powder was washed with copious acetic acid to dissolve any barium carbonate impurity. The acid washed powder was finally dried in oven at ~100 °C to remove the acetic acid.

20

25

Preparation of "in-situ" $\text{FeMn}_4\text{-AB}$ mixed oxide xerogel

2.20 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 6.44 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, and 0.59 g water were dissolved in 20 g ethanol. 0.40 g Acetylene Black was added into the solution and was ultrasonically dispersed. 15 g propylene

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oxide was quickly added into the alcoholic solution under stirring. The solution was stirred for several minutes and then left static overnight. The formed gel was dried in an oven at 50 °C over several days.

5 *Preparation of Metal Oxides by Hydrolysis*

A 0.1M solution of the hydrous metal oxides was stirred rapidly while slowly adding 0.3M NaOH solution. An equal volume amount of 0.3M NaOH solution was added and was sufficient to increase the pH of the hydrous metal oxide solution to >7pH. During the addition of the 0.3M NaOH a precipitate forms and at 7pH, the hydrous metal oxide is completely converted to the oxide form. The precipitated metal oxide is then centrifuged at 3000RPM for 30 minutes. A clear supernatant is decanted and distilled water is added to replace the volume decanted. The precipitated metal oxide is shaken vigorously for several minutes to disperse the metal oxide and wash before being centrifuged a second time. The slightly colored liquid is decanted and the metal oxide was dried in a 100 °C oven for 12 hours.

15

Characterization of Metal Oxides by Hydrolysis

Samples of the oxides were analyzed for composition and surface area. A sample of FeMn₄ was prepared as described above, and the composition analyzed using EDS, as shown in Table 2. All results in weight% and are normalized. The accelerating voltage was 15kV and the live time was 180 seconds.

20

Table 2 Composition of FeMn₄ determined by EDS

	O	Cl	Mn	Fe	Total
Composition	39.0	15.9	36.4	8.7	100.0

BET analysis was performed on several different synthesized samples. All samples were degassed at 50 °C under vacuum for more than 8 hours. The BET surface area was calculated from the adsorption data. The measurements were made using a Micromeritics ASAP 2010. The Fe-Mn aerogel sample was determined to have a surface area of 319 m²/g. The Mn-V

25

aerogel sample was determined to have a surface area of 73 m²/g. The V₂O₅ aerogel was determined to have a surface area of 71 m²/g.

Electrode Fabrication

5 Electrodes for testing were fabricated using the following procedure:

- The metal oxide was ground by hand to a fine powder.
- The conductive component (if used) was added to the oxide powder and ground again.
- Approximately 20mg of the powder was added to a mortar, then the appropriate
10 amount of binder was added from a 5% in solvent mixture.
- Approximately 150mg of 1-methyl-2-pyrrolidinone (NMP) was added.
- The mixture was again ground to form a paste. The paste was then applied to the collector substrate (stainless steel in most examples).
- The metal oxide on stainless steel electrode was then heated for 1 hour at 100C
15 until all solvents evaporated.
- A Nylon filter disc was then placed over the dried metal oxide electrode. The electrode/filter disc assembly was then placed in the electrochemical apparatus for measurement.

20 The filter disc is used to ensure the electrode stays in place in the test cell. The filter disk has sufficient porosity that it should not alter the diffusion of charge or electrolyte. Several different conductive media were used, including acetylene black (AB), Ketjen black (KB), multi-wall carbon nanotubes (CNT), polypyrrole doped onto TiO₂, and polypyrrole mixed with carbon black. The active area of the Ni current collectors used for aqueous measurements is
25 approximately 1 cm², while the active area of the stainless steel collectors used for all non-aqueous measurements is approximately 1.12 cm².

Another important physical property of the electrode is its porosity. In cases where a significant fraction of the electrode mass is composed of porous carbon, we expect the overall

porosity will be dominated by the porosity of the carbon. As an example of this, we have measured thickness for several electrodes. For an electrode with measured thickness 50 microns, the volume would be approximately 0.01cm^3 (assuming uniform thickness). For an electrode mass of 2 mg, this would correspond to a density of 0.2g/cm^3 . The 0.5 mg of carbon would have a volume of $\sim 0.5 \times 10^{-3}\text{cm}^3$ assuming density of 1g/cm^3 , and the metal oxide/hydroxide would have a volume of $0.5 \times 10^{-3}\text{cm}^3$ assuming a density of $\sim 3\text{g/cm}^3$. These combine for a volume of 10^{-3}cm^3 , which is $1/10^{\text{th}}$ of the measured volume. This corresponds to a porosity of 90%. In some embodiments of the invention, any of the electrodes described herein can have a porosity of 70% or greater, in some cases 80% or greater, and in some embodiments, 90% or greater.

Prior Art Example 1: Scan Rate Dependence of Vanadium Oxide

We demonstrate the relation between specific capacitance and scan rate for vanadium oxide. Electrodes were fabricated using vanadium oxide synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70 wt% oxide, 25 wt% AB, and 5 wt% binder (Nafion). Figure 2 shows the specific capacitance as a function of voltage scan rate for three electrodes fabricated using vanadium oxide. The measurements were taken at different scan rates for each electrode. The vanadium oxide shows a very large dependence on the voltage scan rate, with the specific capacitance of about 1000F/g at 0.1mV/s, but less than 20F/g at a 1 mV/s scan rate. The likeliest explanation for this behavior is the high resistivity of the vanadium oxide, preventing rapid charge transfer at the fast voltage scan rates.

We demonstrate the relation between specific capacitance and scan rate for vanadium oxide. Electrodes were fabricated using vanadium oxide synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70 wt% oxide, 25 wt% KB, and 5 wt% binder. Figure 3 shows the specific capacitance for electrodes fabricated using vanadium oxide. Each electrode was measured at one or more voltage scan rate. Again, there is a strong dependence on the electrode mass, with specific capacitance increasing with decreasing electrode mass. The data in Figure 3 is also consistent with Figure 2, showing that the specific capacitance also decreases rapidly with

increasing scan rate. The electrodes were fabricated using approximately the same weight fractions of oxide, conductive material and binder.

Prior Art Example 2: Dependence of Vanadium Oxide Weight Fraction

5 We demonstrate the relation between specific capacitance and vanadium oxide weight fraction. Electrodes were fabricated using vanadium oxide synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. Figure 4 presents the specific capacitance for a series of vanadium oxide electrodes, where the weight fraction of oxide was varied systematically. The binder content (Nafion) was 5 wt% for all
10 electrodes. At long times without binder, the vanadium electrode dissolved in the 1M KOH. All capacitance measurements were taken at a 10 mV/s voltage scan rate. The results show the specific capacitance is largest when the electrode is 65% carbon black. Note that using the standard literature practice, the capacitance value for 5% oxide would be reported as 260 F/g.

15 *Prior Art Example 3: Dependence of Vanadium Oxide Weight Fraction*

 We demonstrate the relation between specific capacitance and conductive media for vanadium oxide. Electrodes were fabricated using vanadium oxide synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% conductive media, and 5% binder. The
20 specific capacitance of vanadium oxide electrodes with different types of conductive media (Ketjen black, acetylene black, CNT) is shown in Figure 5. The specific capacitance data, which was taken for a range of electrode masses, and at various voltage scan rates, indicates there is no order-of-magnitude difference between the conductive materials.

25 *Comparative Example 4: Effect of Electrode Mass and Oxide Composition for Aqueous Electrolytes*

 We demonstrate the relation between specific capacitance and electrode mass for several materials of this invention and of the prior art. Multiple electrodes were fabricated using oxides synthesized with the xerogel procedure, using the standard electrode fabrication procedures described
30 previously. The nominal electrode composition is 70% oxide, 25% AB or KB, and 5% binder. All data

is taken at a scan rate of 1.0 mV/sec in 1M KOH. Figure 6 shows the effect of metal oxide composition and electrode mass on the specific capacitance. The electrodes fabricated from the iron-manganese mixed metal oxides have larger specific capacitance than the vanadium oxide-based electrodes. Note that the specific capacitance calculation is based on total electrode mass including the carbon and the binder.

Figure 7 shows the total electrode capacitance as a function of electrode mass for the electrodes presented in Figure 6. In contrast to the specific capacitance which increases with decreasing electrode mass, the total capacitance appears to have a maximum that occurs for electrodes with mass in the range of 1 to 2 mg. This is consistent with the rapid decrease in specific capacitance with electrode mass as shown in Figure 6.

Comparative Example 5: Effect of Electrode Mass and Oxide Composition for Aqueous Electrolytes

We demonstrate the relation between specific capacitance and electrode mass for several materials of this invention and of the prior art. Multiple electrodes were fabricated using oxides synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB or KB, and 5% binder. All data is taken at a scan rate of 10 mV/sec in 1M KOH. Figure 8 shows the effect of metal oxide composition on specific capacitance. The electrodes fabricated from the iron-manganese mixed metal oxides have larger specific capacitance than the vanadium oxide-based electrodes. Note that the specific capacitance calculation is based on total electrode mass including the carbon and the binder.

Example 6: Effect of Electrode Mass and Oxide Composition for Fe-Mn Mixed Metal Oxides in Aqueous Electrolytes

We demonstrate the relation between specific capacitance and electrode mass for several iron-manganese mixed metal oxide compositions. Multiple electrodes were fabricated using oxides synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. All measurements were performed using 1M KOH as the electrolyte. The capacitance as a function

of electrode mass measured at 10 mV/s is given in Figure 9. The capacitance as a function of electrode mass measured at 1 mV/s is given in Figure 10.

Example 7: Effect of Electrode Mass and Oxide Composition for Fe-Mn-Ni-Co Mixed Metal Oxides in Aqueous Electrolytes

We examined the relation between specific capacitance and electrode mass for several iron-manganese oxides. Electrodes were fabricated using oxides synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. All measurements were performed using 1M KOH as the electrolyte. The capacitance as a function of electrode mass measured at 10 mV/s is given in Figure 11. The capacitance as a function of electrode mass measured at 1 mV/s is given in Figure 12.

Example 8: Effect of “In-Situ” Oxide Synthesis of Fe-Mn-Co Measured in Aqueous Electrolytes

A mixed oxide of formula FeMnCo was synthesized using the methods described previously. Multiple electrodes were fabricated from this oxide using the method described previously, with a composition of 70% oxide, 25% acetylene black, and 5% binder. An “in-situ” synthesis of FeMnCo was performed in the presence of carbon black, with a nominal ratio of oxide to carbon black the same as the previous electrode. This material was combined with 5% binder to form a second set electrode of electrodes. A third set of electrodes was formed by combining 70 wt% of the “in-situ” synthesized FeMnCo with 25 wt% AB and 5 wt% binder. The capacitance was measured at 1 mV/s in 1M KOH. Figure 13 presents the measured specific capacitance as a function of electrode mass for all three types of electrode preparation.

Example 9: Effect of “In-Situ” Oxide Synthesis of Fe-Mn₄ Measured in Aqueous Electrolytes

A mixed oxide of formula FeMn₄ was synthesized using the methods described previously. Multiple electrodes were fabricated from this oxide using the method described previously, with a composition of 70% oxide, 25% acetylene black, and 5% binder. An “in-situ” synthesis of FeMn₄ was performed in the presence of AB, with a nominal ratio of oxide to AB the same as the previous electrode. This material was combined with 5% binder to form a second set electrode of electrodes. A third set of electrodes was formed by combining 70 wt% of

the “in-situ” synthesized FeMn₄-AB with 25 wt% AB and 5 wt% binder. The capacitance was measured at 1 mV/s in 1M KOH. Figure 14 presents the measured specific capacitance as a function of electrode mass for all three types of electrode preparation.

5 *Example 10: Effect of “In-Situ” Oxide Synthesis of Fe-Mn₄ Measured in Aqueous Electrolytes*

A mixed oxide of formula FeMn₄ was synthesized using the methods described previously. Multiple electrodes were fabricated from this oxide using the method described previously, with a composition of 70% oxide, 25% acetylene black, and 5% binder. An “in-situ” synthesis of FeMn₄ was performed in the presence of single-wall carbon nanotubes (SWNT), with a nominal ratio of oxide to SWNT the same as the previous electrode. This material was combined with 5% binder to form a second set electrode of electrodes. An “in-situ” synthesis of FeMn₄ was performed in the presence of single-wall carbon nanotubes (SWNT), with a nominal ratio of 5 wt% SWNT to oxide. This material was combined with 5% binder to form a third set electrode of electrodes. A fourth set of electrodes was formed by combining 75 wt% of the “in-situ” synthesized FeMn₄ with 20 wt% AB and 5 wt% binder. The capacitance was measured at 1 mV/s in 1M KOH. Figure 15 presents the measured specific capacitance as a function of electrode mass for all three types of electrode preparation.

20 *Example 11: Effect of Heat Treatment of Hydroxide/Oxide for Aqueous Electrolytes*

The synthesized materials have a high degree of hydroxide character, due to the synthesis and drying conditions. Heating of these materials is known to convert the hydroxide to oxide. We demonstrate the relative contribution of the hydroxide and oxide in aqueous electrolyte in the following manner. Samples of FeMn₄, prepared as described previously, were heat-treated at various temperatures and durations. Electrodes were formed from these oxides using the standard procedure, and standard electrode composition of 70% hydroxide/oxide, 25% AB, and 5% binder. The capacitance was measured at 1 mV/s in 1M KOH, with the following results.

Heat treatment	Electrode mass (mg)	<u>Specific Capacitance</u> F/g
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50 C, 1 day	2	517
100C 2h	0.9	395
150C 2h	1.3	137
200C 2h	1	115
250C 2h	1.6	31

X-ray diffraction studies of the hydroxide/oxide materials before and after heat treatment show the heat treatment leads to a decrease in the amount of hydroxide present and an increase in the amount of oxide as the heat treatment temperature is increased.

5 *Comparative Example 12: Effect of Scan Rate for Aqueous Electrolyte*

We demonstrated the relation between specific capacitance and scan rate for Fe₂Mn₃. An electrode was fabricated using Fe₂Mn₃ synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. Figure 16 shows the specific capacitance as
 10 a function of voltage scan rate for this electrode. For comparison, the data previously shown in Figure 2 is also included. The vanadium oxide shows a very large dependence on the voltage scan rate, while the Fe₂Mn₃ electrode demonstrates much less sensitivity to voltage scan rate.

Example 13: Effect of Scan Rate in Aqueous Electrolyte

15 We demonstrate the relation between specific capacitance and scan rate for FeMn and FeMn₄. Four electrodes were fabricated using FeMn or FeMn₄ synthesized by the standard xerogel process, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. Figure 17 presents the specific capacitance for FeMn and FeMn₄ as a function of voltage scan rate. To ensure there are no artifacts due to the repeated
 20 testing of single electrodes, the FeMn₄ (a) sample was measured from fastest voltage scan rate to slowest, while the FeMn₄ (b) sample was measured starting at the slowest voltage scan rate. Each of the four electrodes was used in measurements at two or more scan rates. Each electrode exhibits the rapid increase in specific capacitance with decreasing voltage scan rate.

25 *Example 14: Effect of Scan Rate for FeMn₄ in Aqueous Electrolyte*

We demonstrate the relation between specific capacitance and voltage scan rate for FeMn₄. Multiple electrodes were fabricated using FeMn₄ synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. Figure 18 shows the specific capacitance for the electrodes.

5 Measurements were taken in 1M KOH.

Example 15: Effect of Conductive Media Weight Fraction in Aqueous Electrolytes

We examined the relation between specific capacitance and AB weight fraction for FeMn₄. Multiple electrodes were fabricated using FeMn₄ synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The oxide content was
10 varied from 65 wt% to 95 wt% with 5 wt% binder. Figure 19 shows the specific capacitance as a function of electrode mass for FeMn₄ with measured at 1 mV/s in 1M KOH.

Example 16: Effect of Binder for Aqueous Electrolytes

15 We demonstrate the relation between specific capacitance and binder polymer for FeMn₄. Multiple electrodes were fabricated using FeMn₄ synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. Figure 20 shows the specific capacitance as a function of binder, for FeMn₄, measured at 1 mV/s in 1M KOH. Additional electrodes were
20 fabricated using an epoxy as the binder or using a silane sol-gel as the binder. The capacitance for both binders was too small to fit on the scale of Figure 20.

Example 17: Effect of Active Species and Molarity, for FeMn₄ in Aqueous Electrolytes

We demonstrate the relation between specific capacitance and KOH molarity for FeMn₄.
25 Multiple electrodes were fabricated using FeMn₄ synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. Testing has been performed in 1M, 2M and 4M KOH, as shown in Figure 21. Capacitance measurements have also been performed using 1M LiOH and 1M KCl, as shown in Figure 21. The low capacitance for KCl suggests the hydroxyl is the active species.

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Example 18: Effect of Active Species and Molarity, for Fe₁Mn₄Ni_{0.5}Co_{0.5} in Aqueous Electrolytes

We demonstrate the relation between specific capacitance and KOH molarity for $\text{Fe}_1\text{Mn}_4\text{Ni}_{0.5}\text{Co}_{0.5}$ oxides. Multiple electrodes were fabricated using $\text{Fe}_1\text{Mn}_4\text{Ni}_{0.5}\text{Co}_{0.5}$ oxides synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. Figure 22 presents the capacitance measured at 1mV/s. Measurement performed using 1M LiOH as the electrolyte gave specific capacitance slightly less than would be expected in 1M KOH.

Example 19: Effect of Additional Salts on FeMn4 in Aqueous Electrolytes

We measured the specific capacitance of FeMn4 in 1M KOH with additional salts. Electrodes were fabricated using FeMn4 synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Measurements were performed using 1M KOH in conjunction with different salts. At 10 mV/s, 1M KOH with 1M NaHSO_3 the capacitance was diminished, but was reasonably stable for 100 voltage cycles. 1M KOH with 1M NaSCN was not stable under cycling, neither was 1M KOH with 1M K_2CO_3 .

Example 20: Effect of Electrode Mass and Oxide Composition for Nickel-Cobalt Mixed Metal Oxides in Aqueous Electrolytes

We demonstrated the relation between specific capacitance and electrode mass for several nickel-cobalt oxides of varying composition. Electrodes were fabricated using oxides synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. All data is taken in at 10 mV/s in 1M KOH. The specific capacitance measured on the fifth voltage cycle is given in below.

	Specific Capacitance (F/g)	Electrode mass (mg)
Ni	367	1.1

Ni ₄ Co	541	0.9
Ni ₂ Co	614	0.7
NiCo	674	0.9
NiCo ₂	56	1.6
NiCo ₃	36	1.6

Example 21: Effect of Electrode Mass and Oxide Composition for Nickel-Cobalt Mixed Metal Oxides in Aqueous Electrolytes

We demonstrate the relation between specific capacitance and oxide composition for several nickel-cobalt oxides doped with various amounts of iron and/or manganese. Electrodes were fabricated using oxides synthesized with the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. Data was taken at 10 mV/s and 1 mV/s in 1M KOH.

NiFe and NiMn were both synthesized as described previously, and electrodes were fabricated. For both electrodes, the capacitance was not stable, decreasing rapidly with cycling.

Electrodes were fabricated using the following oxides, NiCo₂Fe_{0.1}, NiCo₂Fe_{0.5}, Ni₁Co₂Fe_{1.0}, Ni₁Co₂Fe_{1.0}Mn_{0.5}, Ni₁Co₂Fe_{0.5}Mn_{0.5}. The nominal electrode composition is 70% oxide, 25% AB, and 5% binder. Data was taken at 10 mV/s and 1 mV/s in 1M KOH. The electrodes underwent voltage cycling until the capacitance appeared steady from one cycle to the next. All electrodes had large capacitance at both voltage scan rates. Ni₁Co₂Fe_{1.0}Mn_{0.5} had the largest specific capacitance at both scan rates

Example 22: Effect of Electrode Mass and Oxide Composition for FeMn₄ Mixed Metal Oxides in Non-Aqueous Electrolytes

We demonstrate the specific capacitance of FeMn₄ in non-aqueous electrolytes. Electrodes were fabricated using FeMn₄ synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode

composition was 70% oxide, 25% AB, and 5% binder. Testing was performed with three different electrolytes (Figure 23) at various scan rates. LiPF₆ was the salt used in all the measurements. The straight lines on the Figure are given to indicate the rate of change of capacitance with voltage scan rate. . Visual examination of the system during testing revealed
5 no indication of the formation of hydrogen gas, as would be evidenced by bubbling. The electrode was cycled repeatedly and was very stable at 1.8V. Measurements were also performed using electrodes fabricated from the heat-treated samples of Example 11. There was little difference in measured specific capacitance for the heat-treated samples, as opposed to the case in aqueous electrolytes.

10
Example 23: Effect of Electrode Mass and Oxide Composition for FeMn₄ Mixed Metal Oxides in Non-Aqueous Electrolytes

We measured the specific capacitance of FeMn₄ in non-aqueous electrolytes. Electrodes were fabricated using FeMn₄ synthesized by the xerogel procedure, using the standard electrode
15 fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Testing was performed with EC/PC (50/50) as the solvent, using LiPF₆ and LiBF₄ at various molarities. The testing has been performed at several different scan rates. The results are shown in Figure 24. The capacitance of these samples appears to be stable under cycling, with 100 cycles or more showing no change in capacitance.

20
Example 24: Effect of Electrode Mass and Oxide Composition for FeMn₄ Mixed Metal Oxides in Non-Aqueous Electrolytes

We measured the specific capacitance of FeMn₄ in non-aqueous electrolytes. Electrodes were fabricated using FeMn₄ synthesized by the xerogel procedure, using the standard electrode
25 fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Testing was performed with EC/PC (20/80) as the solvent, using LiPF₆ and LiBF₄ at various molarities. The testing has been performed at several different scan rates. The results are shown in Figure 25. The capacitance of these samples appears to be stable under cycling, with 100 cycles or more showing no change in capacitance.

Example 25: Effect of Electrode Mass and Oxide Composition for FeMn4 Mixed Metal Oxides in Non-Aqueous Electrolytes

We measured the specific capacitance of FeMn, FeMn4, and FeMn8 in 1M LiBF₄ in EC/PC (80/20). Electrodes were fabricated using FeMn, FeMn4, and FeMn8 synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Testing was performed at various voltage scan rates. The measured specific capacitance as a function of voltage scan rate is given in Figure 26, for FeMn1, FeMn4, and FeMn8.

Example 26: Interfacial Stability Testing in Aqueous Electrolyte

We have performed initial examination of the interface (surface-electrolyte) stability of the capacitance response in aqueous electrolytes. Initial measurements were performed using FeMn₄ in 1M KOH. Measurements showed the capacitance decreased under repeated cycling, losing up to 80% of the capacitance over 25 cycles. Similar behavior is observed in the Fe_xMn_yNi_zCo₆ electrodes, although the rate of change in the capacitance may be slower. There are several possible reasons for this decrease in capacitance, including the physical loss of the hydroxide/oxide from the electrode due to stress and the conversion of the hydroxide/oxide to more crystalline oxide. We have performed a series of experiments to explore the origins of this behavior and identify ways to mitigate it moving forward. The results can be summarized in the following points.

1. Measurement of the capacitance under limited cycling conditions was performed using constant current and constant voltage scan rate methods. The results showed the decrease in capacitance was similar at both 10 mV/s and 1 mV/s voltage scan rates.
2. Electrodes were fabricated using higher binder content to improve adhesion of the oxide. The starting capacitance was lower, due to the higher binder content preventing access of the electrolyte to the oxide surface. Measurement of the capacitance showed a similar rate of decrease during cycling.
3. XRD measurements performed on the electrode materials before and after the electrochemical cycling indicated an increase in crystallinity of the sample that had undergone the cycling testing.

4. The decrease in capacitance is slower for FeMn₄ synthesized using a hydrolysis method as opposed to FeMn₄ synthesized using the xerogel synthesis method. XRD measurements have shown the metal oxide created using a hydrolysis synthesis method has lower initial crystallinity. However, the performance of electrodes fabricated with either type of FeMn₄ shows substantial degradation in the capacitance during cycling in an aqueous electrolyte.
5. Use of KCl in water as the electrolyte results in lower specific capacitance, but the capacitance appears more stable under limited cycling. We believe the Cl ions do not react at the surface, but instead, the specific capacitance arises solely from the double layer mechanism.
6. We performed initial experiments where additional salts were included in the 1M KOH electrolyte, including salts such as NaHSO₃, NaSCN, or K₂CO₃. The resulting capacitance measurements in most cases showed no substantial difference in the capacitance or stability of the capacitance.

We have also performed a series of experiments to better understand how the oxide/hydroxide composition affects the cycling stability of the measured capacitance. These experiments were conducted by altering the composition of the metal oxide/hydroxide, and measuring the change in the capacitance under constant voltage scan rate conditions, with the following results.

1. Mn appears to have the largest difficulties with stability at high pH.
2. Various compositions of Ni and Co have shown much better cycling stability, while MnNi was not stable under cycling. The capacitance of NiCo was measured >900 F/g at 0.1 mV/s. The capacitance of Ni₂Co decreased by less than 2% over the course of 15 voltage sweeps.
3. Addition of small amounts of Fe or Mn to the NiCo compounds did not substantially alter the capacitance or stability.
4. FeNi was stable but had low capacitance.

Example 27: Interfacial Stability Testing in Non-Aqueous Electrolyte

We demonstrated the stability of the specific capacitance of FeMn4 in non-aqueous electrolytes. Electrodes were fabricated using FeMn4 synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Testing was performed with EC/PC (20/80) as the solvent, using with 0.1M LiPF₆. The testing has been performed using galvanic cycling at a current density of 0.1A/g. The capacitance was measured at 329F/g during the 4th cycle, and 332 F/g during the 15th cycle. Other measurements showed the capacitance to be stable for 100 cycles after some initial fluctuation due to interface stabilization.

Example 28: Interfacial Stability Testing in Non-Aqueous Electrolyte

We demonstrated the stability of the specific capacitance of FeMn4 in non-aqueous electrolytes. Electrodes were fabricated using FeMn4 synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Testing was performed with EC/PC (20/80) as the solvent, using with 0.1M LiPF₆. The specific capacitance was measured at a voltage scan rate of 0.1 mV/s. The specific capacitance was measured to be 587 F/g on the 5th voltage cycle.

Example 29: Interfacial Stability Testing in Non-Aqueous Electrolyte

We demonstrated the stability of the specific capacitance of FeMn4 in non-aqueous electrolytes. Electrodes were fabricated using FeMn4 synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Testing was performed with EC/PC (50/50) as the solvent, using with 0.1M LiPF₆. The specific capacitance was measured at a voltage scan rate of 1.0 mV/s. Figure 27 shows the cyclic voltammetry response of the electrode for the first 50 voltage cycles. All the variation in the response depicted in the figure comes in the first 14 cycles. After that, the response lies on a single curve. This is also shown in Figure 28, which shows the specific capacitance as a function of voltage cycle number. This figure demonstrates that after a number of equilibration cycles, the specific capacitance is very stable

Example 30: Interfacial Stability Testing in Non-Aqueous Electrolyte

We demonstrated the stability of the specific capacitance of FeMn₄ in non-aqueous electrolytes. Electrodes were fabricated using FeMn₄ synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Testing was performed with EC/PC (20/80) as the solvent, using with 2.5M LiPF₆. The electrode was first pre-charged at a current density of 0.28mA. The specific capacitance was then measured at a voltage scan rate of 0.5 mV/s. It was found that the number of voltage cycles needed before equilibration was reduced. However, cycling stability was unchanged.

10 *Example 31: Full-Cell Measurement of Specific Capacitance in Non-Aqueous Electrolyte*

We demonstrated the stability of the specific capacitance of FeMn₄ in non-aqueous electrolytes. Electrodes were fabricated using FeMn₄ synthesized by the xerogel procedure, using the standard electrode fabrication procedures described previously. The nominal electrode composition was 70% oxide, 25% AB, and 5% binder. Testing was performed with EC/PC (50/50) as the solvent, using with 1.0M LiPF₆. The specific capacitance was measured at a voltage scan rate of 1.0 mV/s, using a symmetric full-cell testing configuration. Figure 29 shows the CV response of the system. The specific capacitance of a single electrode was determined to be 28 F/g.

20 *Example 32: Enhancement of Power Density in Non-Aqueous Electrolyte*

The power density of a symmetric supercapacitor is limited by the volume of non-aqueous electrolyte. The reason for the large electrolyte volume is the electrolyte must contain sufficient cations or anions to fully saturate the electrode. The electrolyte can be more than 2/3 of the total cell volume even at 3M concentration. One major factor limiting the salt molarity in non-aqueous electrolytes is the mass of the salt, particularly the anion. For a salt such as LiPF₆, with molecular weight of 152, the Li⁺ cation contributes only 7amu to this mass.

Comparison of the CV curves from half-cell and full cell testing using LiPF₆ or LiBF₄ in EC/PC blends demonstrates that the primary capacitance mechanism in these non-aqueous electrolytes is not reduction/oxidation of the metal oxide, but is due to a combination of double layer formation by the Li⁺ and/or intercalation of the Li⁺. Due to its size, the BF₄⁻ or PF₆⁻ anion contributes little to the voltage of the cell.

A symmetrical supercapacitor with higher power density in non-aqueous electrolytes can be made in the following fashion. Two electrodes are prepared using FeMn₄ or other metal oxides described herein. Each of the two electrodes is placed into a half-cell electrochemical testing device, using the same solvent and salt to be used for the supercapacitor. Each of the two electrodes is tested using galvanic cycling until the measured capacitance has stabilized. The galvanic cycling of each electrode is then halted at the point where it is approximately half-charged and each electrode is removed from the test cell. The Li associated with the electrode from the charging will be removed with the electrode.

The supercapacitor is then formed using both partially charged electrodes, with a new amount of the electrolyte solution. The supercapacitor can be formed with less electrolyte than would be used in a conventional device. When formed, there is no potential difference between the electrodes. When voltage is applied across the electrodes, the Li will dissociate from one electrode and move through the electrolyte to the second electrode. At maximum voltage, there will be no Li cations associated with one electrode while the second electrode has approximately been saturated with Li. This supercapacitor required less electrolyte volume because the electrolyte does not contain all the Li used in the system. Instead, the electrolyte facilitates the transfer of Li from one electrode to the other, and so a smaller electrolyte volume is possible. The potential difference between the two electrodes will be slightly smaller than would exist for the conventional supercapacitor, but the power density will be substantially larger.

Analysis of Specific Capacitance

The specific capacitance is a function of the composition of the electrode. We analyzed the capacitance for several sets of electrodes discussed earlier to understand how composition is related to measured performance. Table 3 summarizes the measured capacitance for electrodes with iron-manganese oxides, using Nafion as the binder (5 wt%) and AB as the conductive material. All data was measured in 1M KOH at 10 mV/s.

Table 3.

Oxide	Sample Wt	Specific Cap F/g	Oxide wt	Oxide Vol.	CB Wt	CB Vol.	Binder Weight	Binder Vol.	Fe/Mn
-------	-----------	------------------	----------	------------	-------	---------	---------------	-------------	-------

Fe2Mn1	0.9	218	0.63	0.188	0.225	0.112	0.045	0.028	2
Fe1Mn1	0.95	192	0.665	0.2	0.2375	0.119	0.0475	0.03	1
Fe1Mn1	0.9	131	0.63	0.189	0.225	0.112	0.045	0.028	1
Fe2Mn3	0.85	284	0.595	0.179	0.212	0.106	0.0425	0.027	0.67
Fe2Mn3	0.3	245	0.21	0.063	0.075	0.037	0.015	0.0095	.67
Fe2Mn3	1.5	287	1.05	0.317	0.375	0.187	0.075	0.047	.67
Fe2Mn3	2.6	234	1.82	0.549	0.65	0.325	0.13	0.082	.67
Fe2Mn3	5.6	181	3.92	1.1825	1.4	0.7	0.28	0.178	.67
Fe1Mn2	1	299	0.7	0.212	0.25	0.125	0.05	0.0316	.5
Fe1Mn3	1	254	0.7	0.213	0.25	0.125	0.05	0.0316	.33
Fe1Mn4	1.1	308	0.77	0.234	0.275	0.138	0.055	0.0348	.25
Fe1Mn4	1.1	356	0.77	0.234	0.125	0.062	0.055	0.035	.25

Analysis of the results shows the specific capacitance can be approximated as:

For Fe2Mn3

$$\text{Specific capacitance} = -19109 (\text{oxide weight}) + 53285 (\text{carbon black volume}) + 278.5$$

5 For other mole ratios

$$\text{Specific capacitance} = 17748.6 (\text{sample weight}) - 339567 (\text{binder volume}) - 463.0357$$

All r values are above 0.9

Similar analysis can be applied to other sets of data, leading to the following relations

For FeMn4 with PTFE binder

$$10 \quad \text{Specific capacitance} = -1689.9 (\text{oxide weight}) + 1151.7 (\text{sample weight}) + 604.3 \quad r = 0.92$$

For Fe2Mn3 with Nafion binder at 1 mV/s

$$\text{Specific capacitance} = -1532.9 (\text{sample weight}) + 1728.1 (\text{oxide volume}) + 252.7 \quad r = 0.93$$

Effect of Calcination

The effect of calcinations was observed by taking a XRD measurement of samples dried
 15 at 50°C (Figure 30) and 100°C (Figure 31). Comparison of the results shows with increasing
 drying temperature, more Mn(OH)₃Cl transformed into Mn₃O₄. The heat-treated samples were
 also investigated using IR analysis, with the results shown in Figure 32. As seen in the Figure,
 increasing the temperature from 50°C to 200°C reduced the area of the hydroxyl peak, although
 a very sharp absorption peak remains. The sample heat treated at 250°C no longer exhibits this
 20 sharp peak, but the spectrum may indicate the presence of adsorbed water. Qualitatively there is
 agreement between the XRD and IR results, with the amount of hydroxyl decreasing with
 increasing temperature.

What is claimed:

1. A capacitor comprising: an electrode, and wherein the electrode comprises: a metal oxide comprising Mn and Fe in a molar ratio of 3:1 to 5:1.
2. The capacitor of claim 1 wherein the electrode comprises Mn and Fe in a molar ratio of 3.5:1 to 4.5:1.
3. The capacitor of any of claims 1-2 wherein the transition metals in the metal oxide consist essentially of Mn and Fe.
4. The capacitor of any of claims 1-3 wherein the metal oxide is characterizable by an absorption band in the infrared region between 1000 and 1100 cm^{-1} .
5. The capacitor of any of claims 1-4 wherein the electrode comprises 5 weight % or less of binder.
6. The capacitor of any of claims 1-5 wherein the electrode further comprises carbon.
7. The capacitor of any of claims 1-6 wherein the electrode has a mass in the range of 0.1 to 2 mg.
8. The capacitor of claim 7 wherein the electrode comprises a specific capacitance of at least 500 F/g if measured at 1 mV/s in 1M KOH aqueous electrolyte.
9. The capacitor of any of claims A-A8 wherein the electrode comprises 40 to 80 weight% metal oxide nanoparticles and 15 to 60 weight% carbon.
10. The capacitor of any of claims 1-9 wherein the electrode comprises at least 5 weight% carbon nanotubes.
11. The capacitor of any of claims 1-10 wherein the metal oxide further comprises Ni, Co, or a combination of Ni and Co.
12. The capacitor of any of claims 1-11 characterizable by an x-ray diffraction spectrum in which the peaks due to a crystalline hydroxide compound are larger than the peaks due to crystalline oxide compounds.

13. A capacitor comprising: an electrode, and wherein the electrode comprises: a metal oxide comprising Ni, Co, and Fe; wherein the Ni and Co are present in a Ni/Co molar ratio in the range of 0.5 to 2 and Fe and Ni are present in a Ni/Fe molar ratio in the range of 1.0 to 10.

14. The capacitor of claim 13 wherein the electrode further comprises Mn.

5 15. A capacitor comprising: a first electrode of any of claims 1-14; an electrolyte; a second electrode; and a circuit that can form an electrical pathway between the first electrode and the second electrode.

16. The capacitor of claim 15 wherein the electrolyte is a nonaqueous liquid

10 17. The capacitor of any of claims 15-16 wherein the first and second electrodes have substantially the same composition.

18. A solar energy system comprising the capacitor of any of claims 15-17 and a photovoltaic cell.

19. A method of making an electrode, comprising:

forming a composition comprising Mn and Fe in a molar ratio of 3.5:1 to 4.5:1;

15 reacting the composition to form a gel comprising Mn and Fe in a molar ratio of 3.5:1 to 4.5:1;

drying the gel to obtain a powder comprising Mn and Fe in a molar ratio of 3.5:1 to 4.5:1; and

compacting the powder to form an electrode.

20. The method of claim 19 wherein the step of drying the gel is conducted in the presence of supercritical CO₂.

20 21. The method of claim 19 wherein the step of reacting comprises reaction with an epoxide.

22. The method of any of claims 19-21 wherein the temperature of the process never exceeds 200 °C.

23. A capacitor, comprising: two electrodes; an electrolyte between the electrodes; wherein the electrolyte comprises a Li salt in a carbonate solution, wherein the carbonate solution comprises 10-30% ethylene carbonate and 70-90% propylene carbonate.

24. The capacitor of claim 23 wherein the carbonate solution comprises 15-25% ethylene
5 carbonate and 75-85% propylene carbonate.

25. The capacitor of any of claims 23-24 wherein the Li salt comprises LiBF_4 , LiPF_6 or a combination of LiBF_4 and LiPF_6 .

26. The capacitor of any of claims 23-25 wherein at least one of the electrodes comprises metal oxide nanoparticles in a carbon matrix.

10 27. The capacitor of any of claims 23-26 further comprising a porous polymeric separator disposed between the electrodes.

28. The capacitor of claim 26 wherein the metal oxide comprises vanadium oxide, iron oxide, iron-manganese oxide, iron-nickel oxide, iron-copper oxide, cobalt-manganese oxide, manganese-titanium oxide, BaFeO_4 , or combinations thereof.

15 29. A method of making the capacitor of claim 23, comprising: providing two electrodes; providing an electrolyte between the electrodes; wherein the electrolyte comprises a Li salt in a carbonate solution, wherein the carbonate solution comprises 10-30% ethylene carbonate and 70-90% propylene carbonate.

30. A method of storing energy comprising: applying a potential to the capacitor of any of
20 claims 1-17 and 23-28 and removing the potential; and wherein, after the potential is removed, an electrical potential persists between the electrodes.

31. A method of making a capacitor, comprising: providing a carbon electrode in a first Li-containing solution; intercalating Li into the electrode to form a Li-intercalated electrode; removing the electrode from the first Li-containing solution; and placing the Li-intercalated
25 electrode into a second Li-containing solution.

32. A method of making an electrode, comprising:

forming a solution comprising carbon particles and a dissolved metal compound;

reacting the metal compound to form a gel;

converting the gel into metal oxide nanoparticles;

5 combining the metal oxide nanoparticles with a binder; and

compacting the metal oxide nanoparticles and binder into an electrode.

33. The method of claim 32 wherein the solution comprises Mn and Fe in a molar ratio of 3:1 to 5:1. .

34. The method of claim 32 wherein the solution is gelled by the addition of an epoxide.

10 35. The method of claim 32 wherein the solution comprises Mn, Co and Fe.

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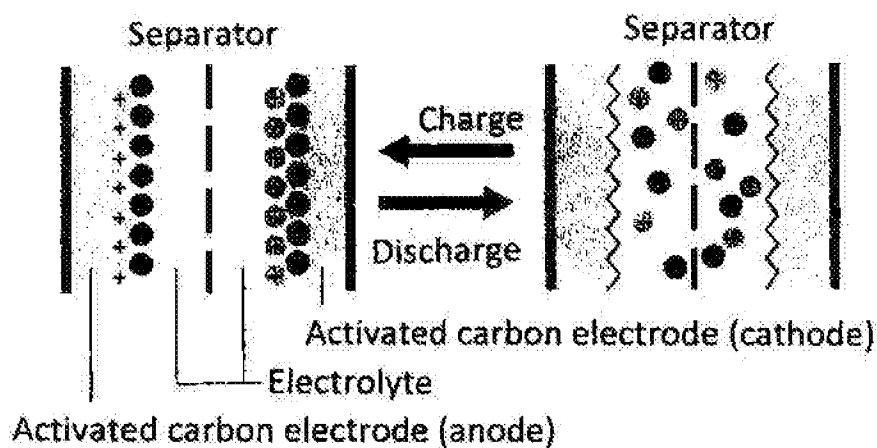
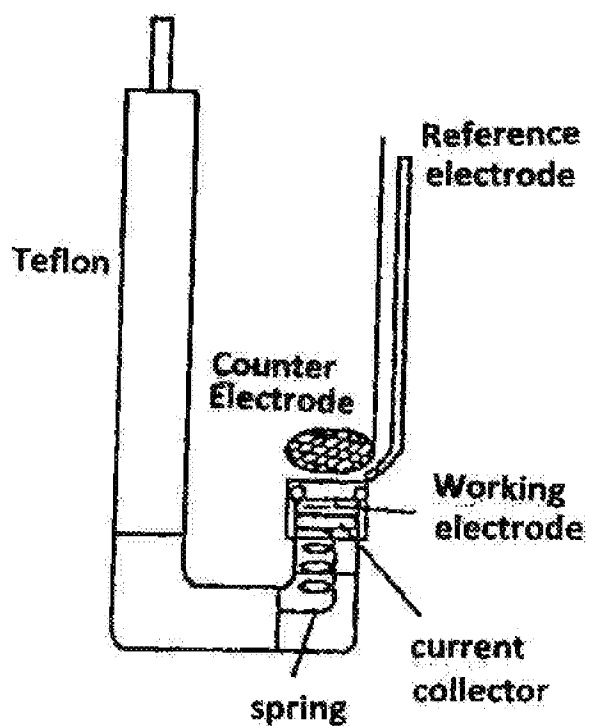


Fig. 1A



Half cell design

Fig. 1B

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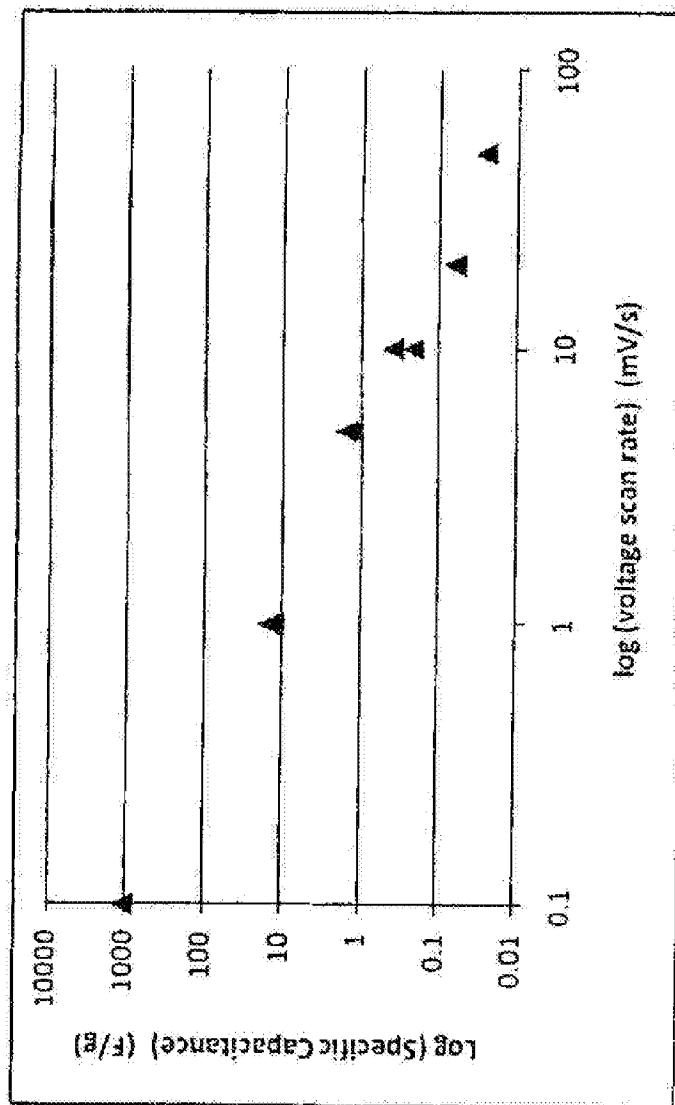


Fig. 2

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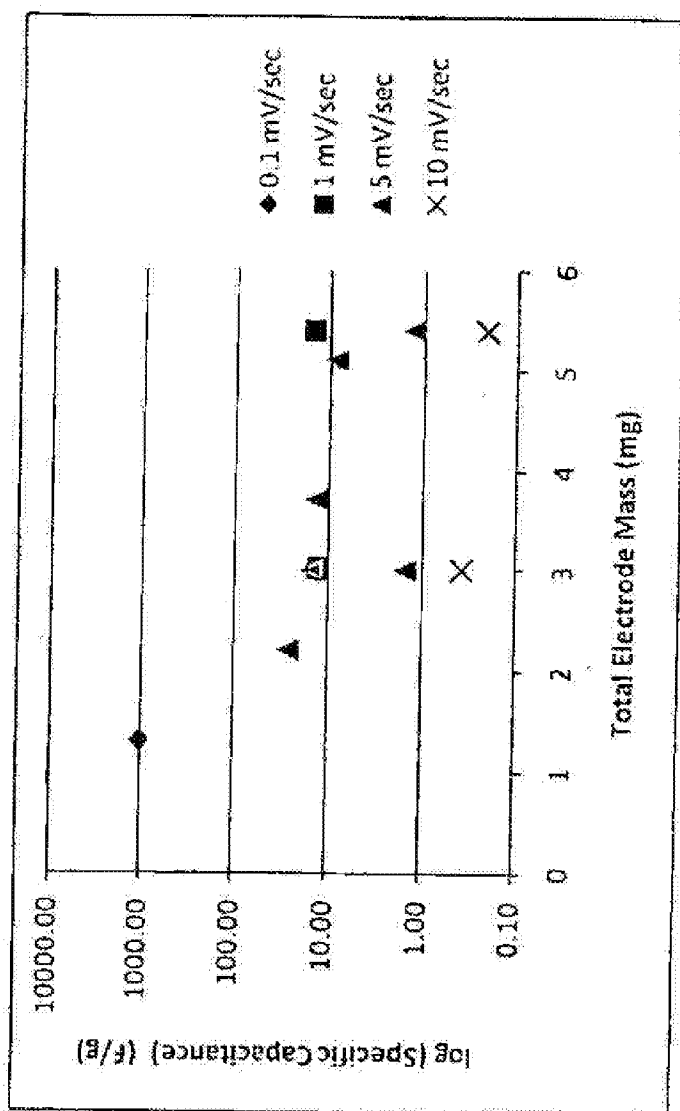


Fig. 3

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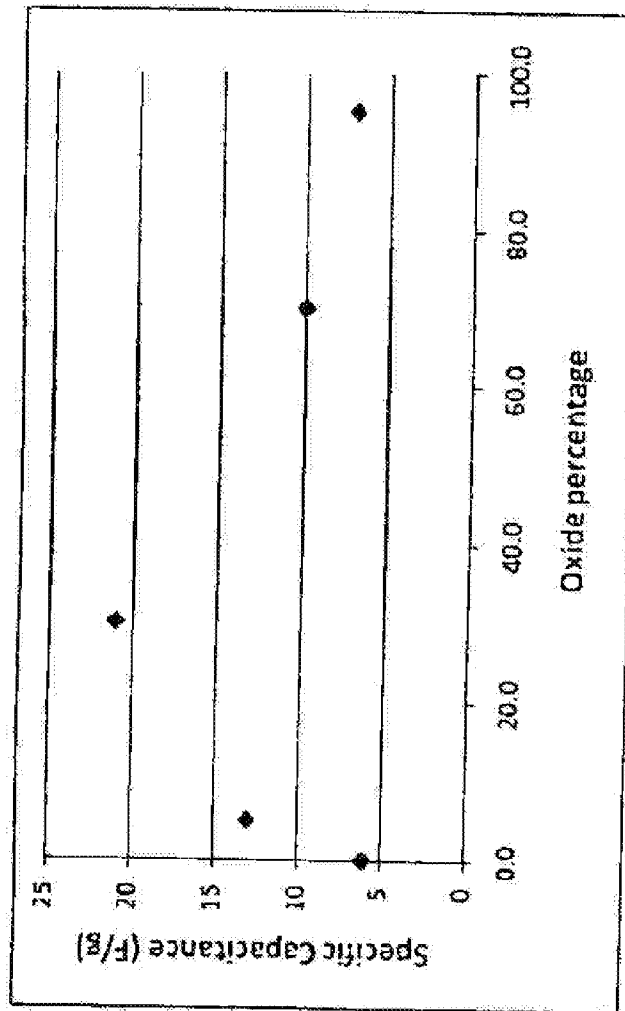


Fig. 4

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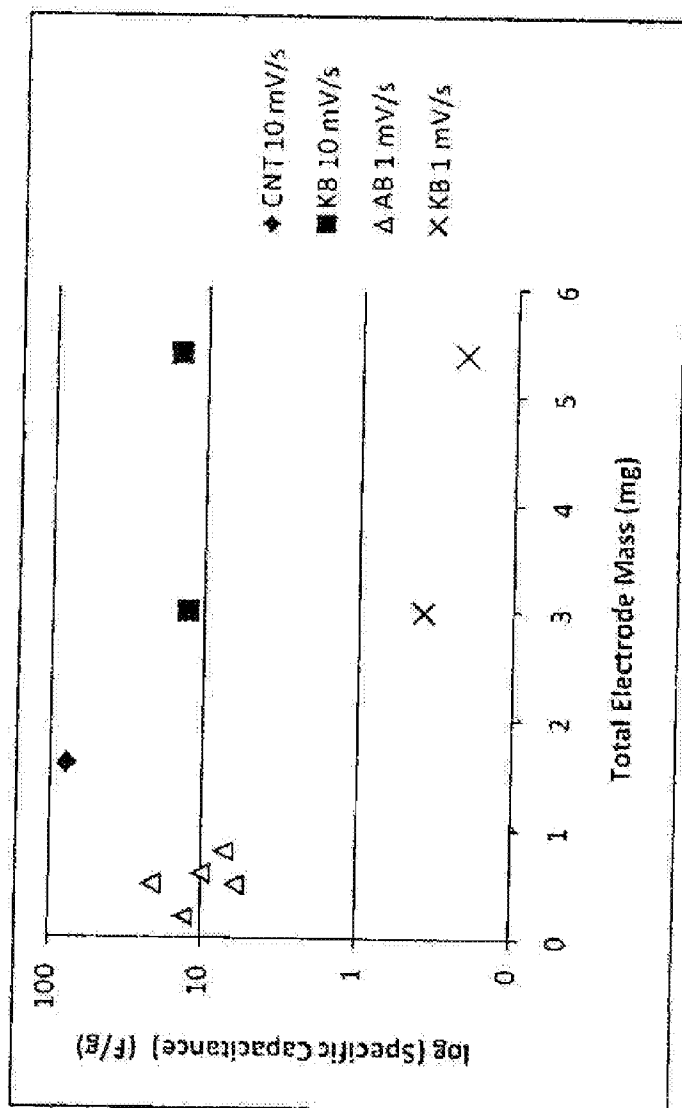


Fig. 5

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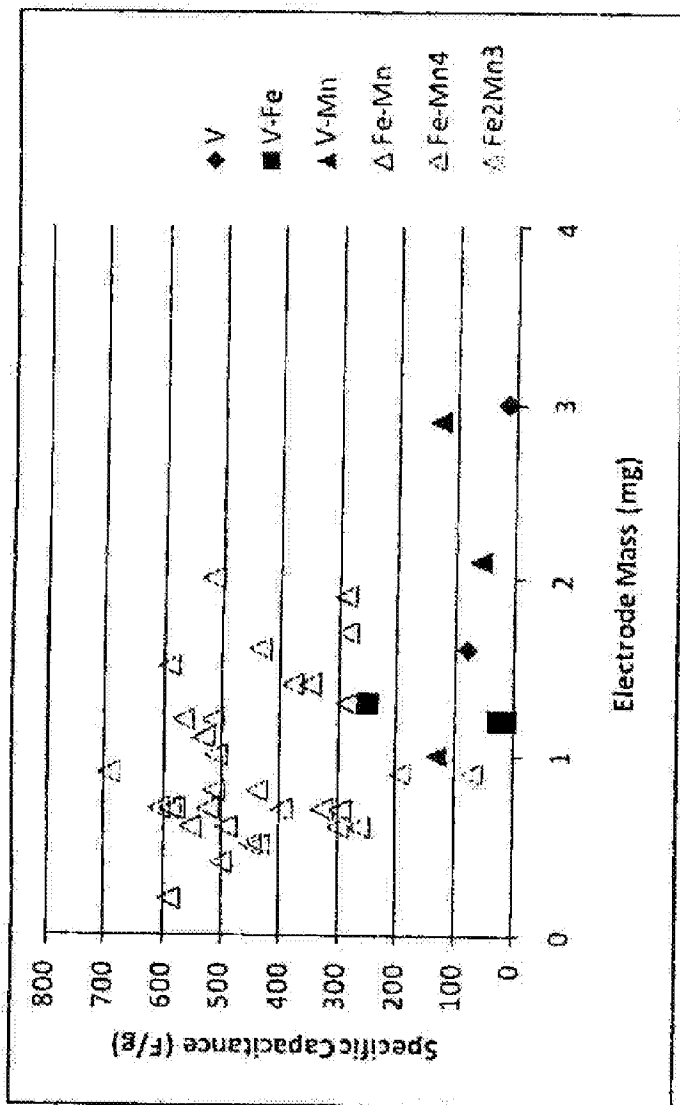


Fig. 6

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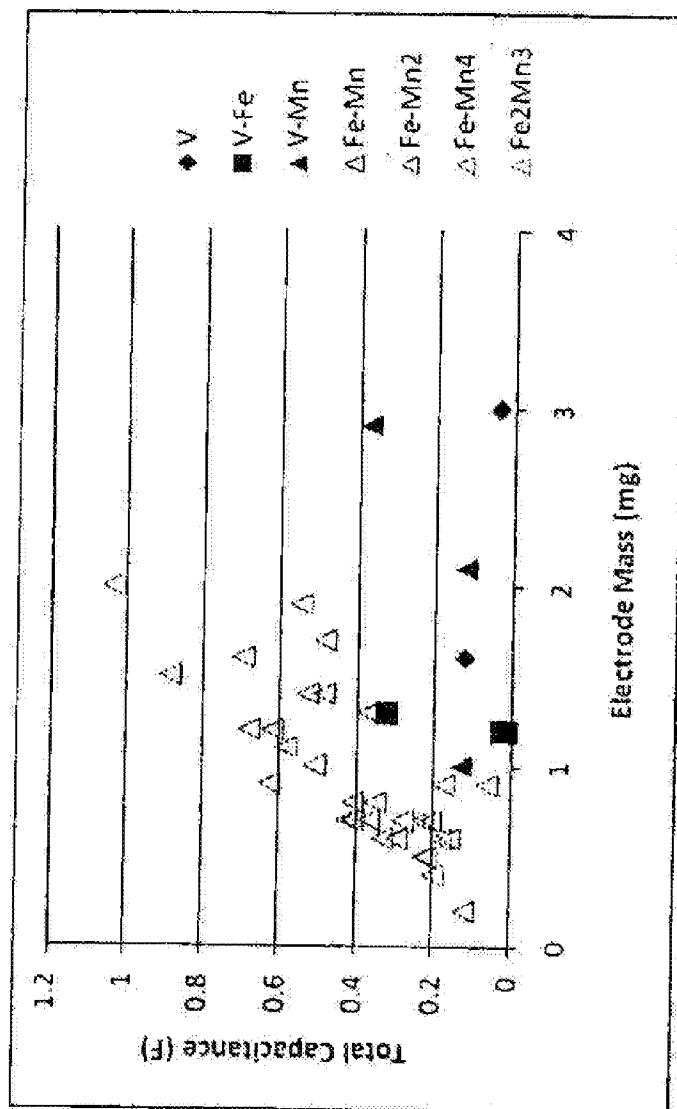


Fig. 7

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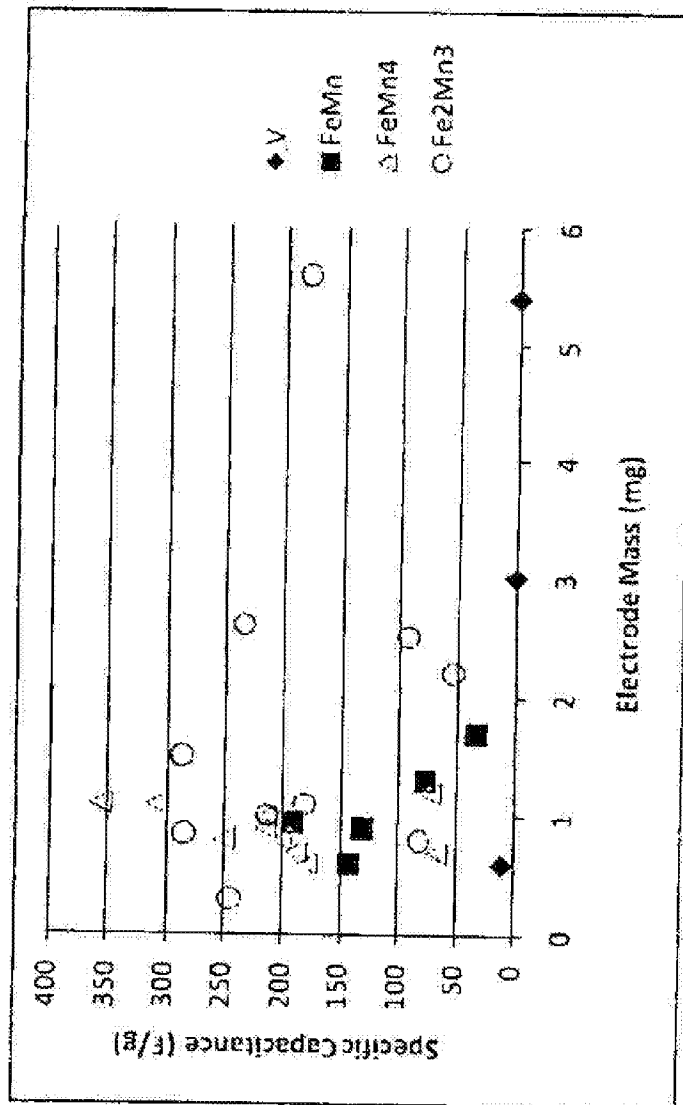


Fig. 8

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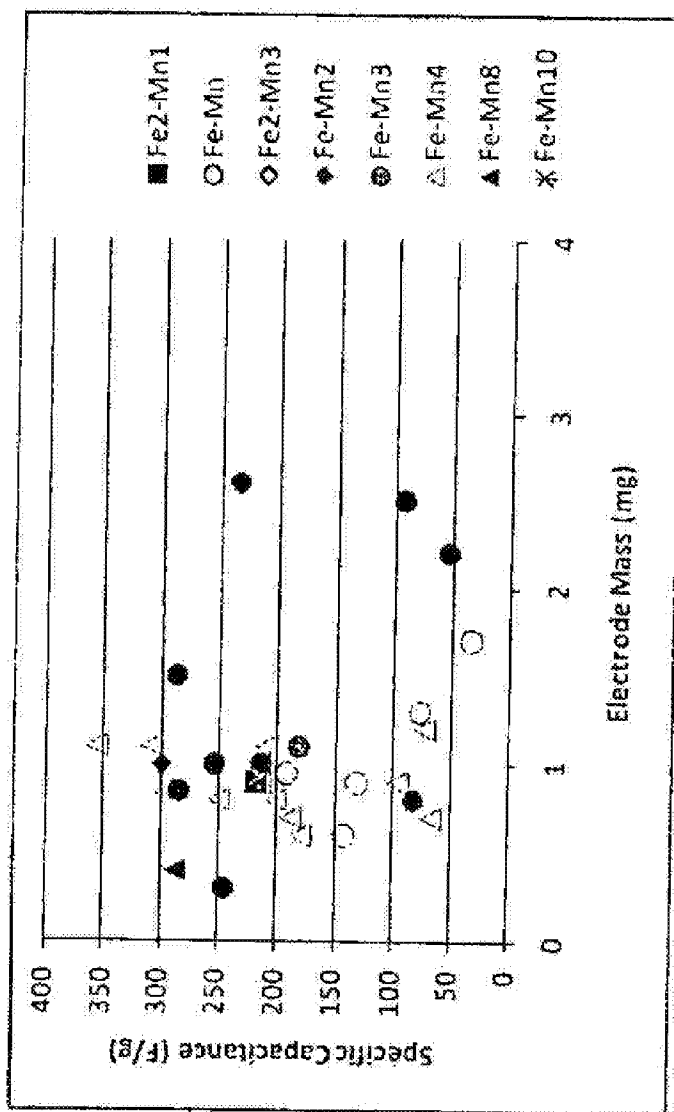


Fig. 9

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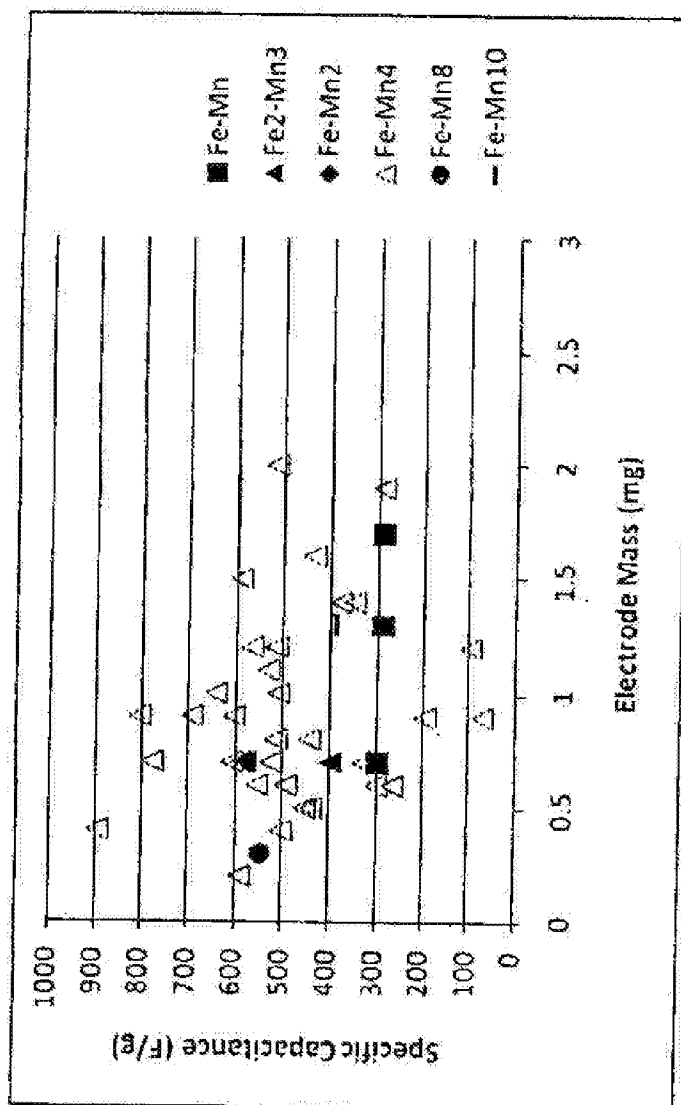


Fig. 10

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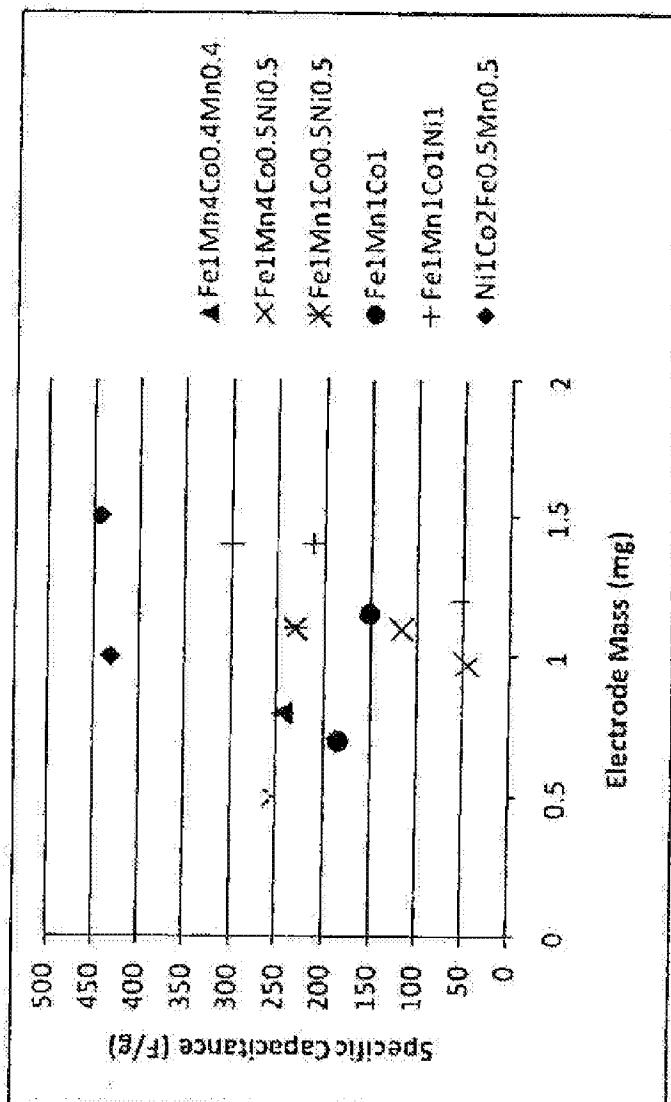


Fig. 11

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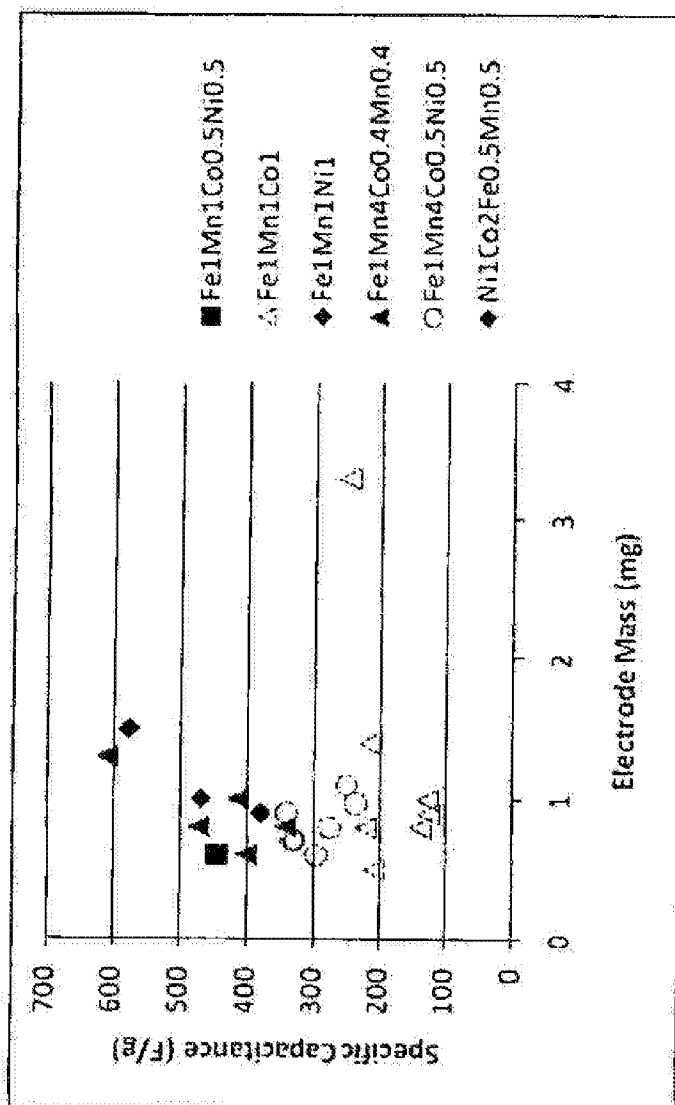


Fig. 12

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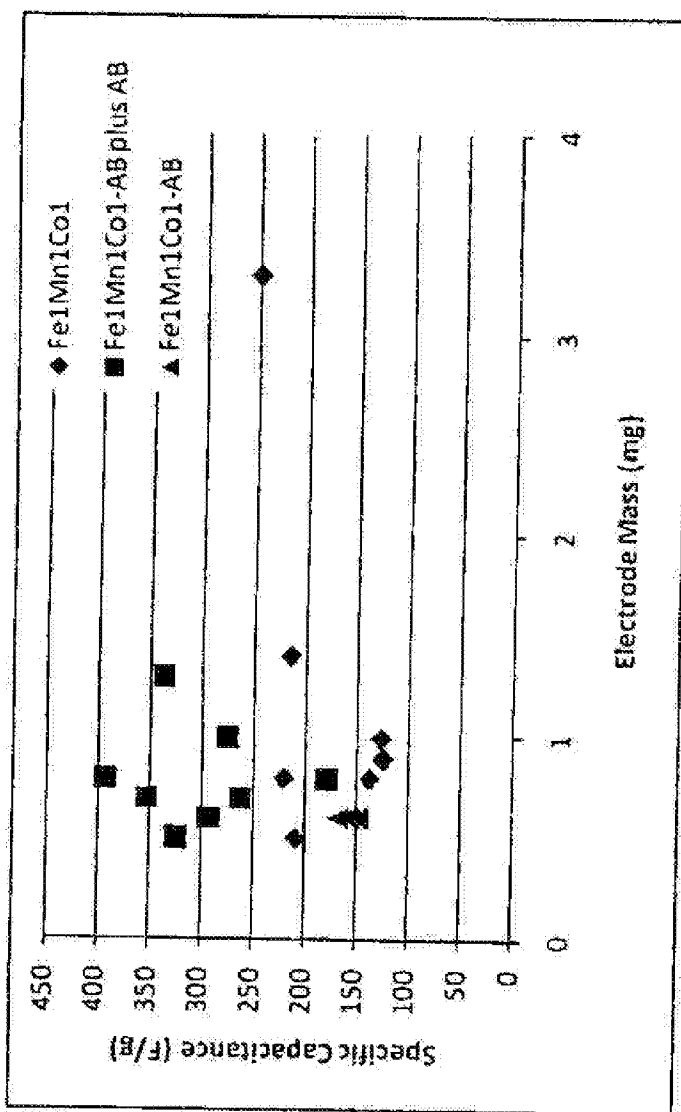


Fig. 13

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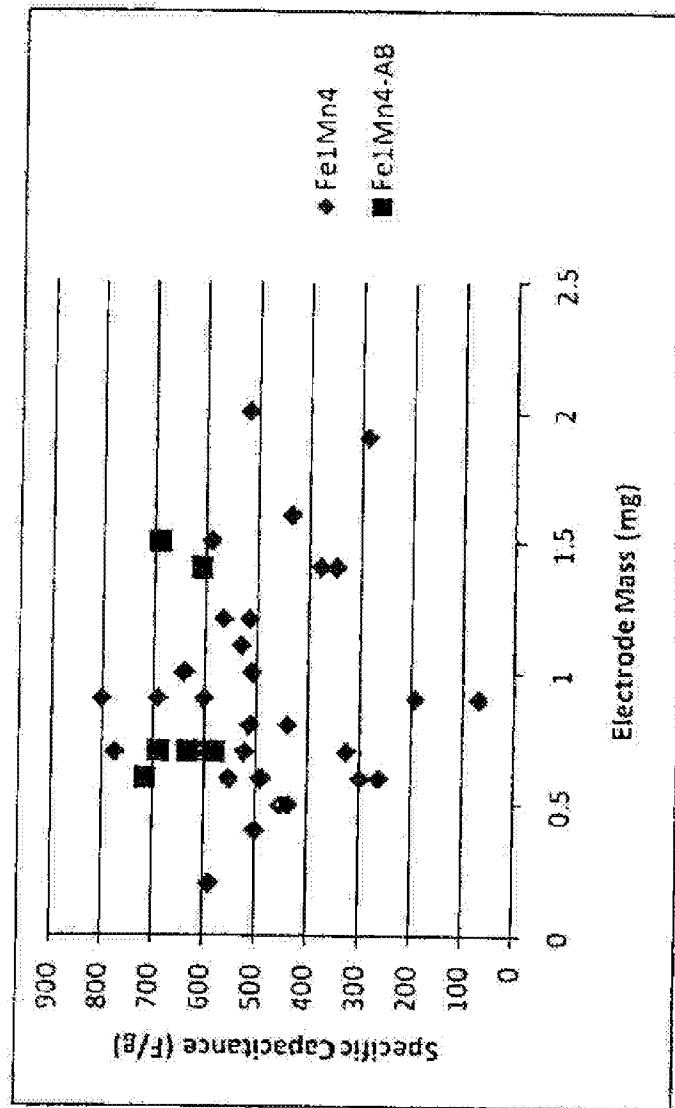


Fig. 14

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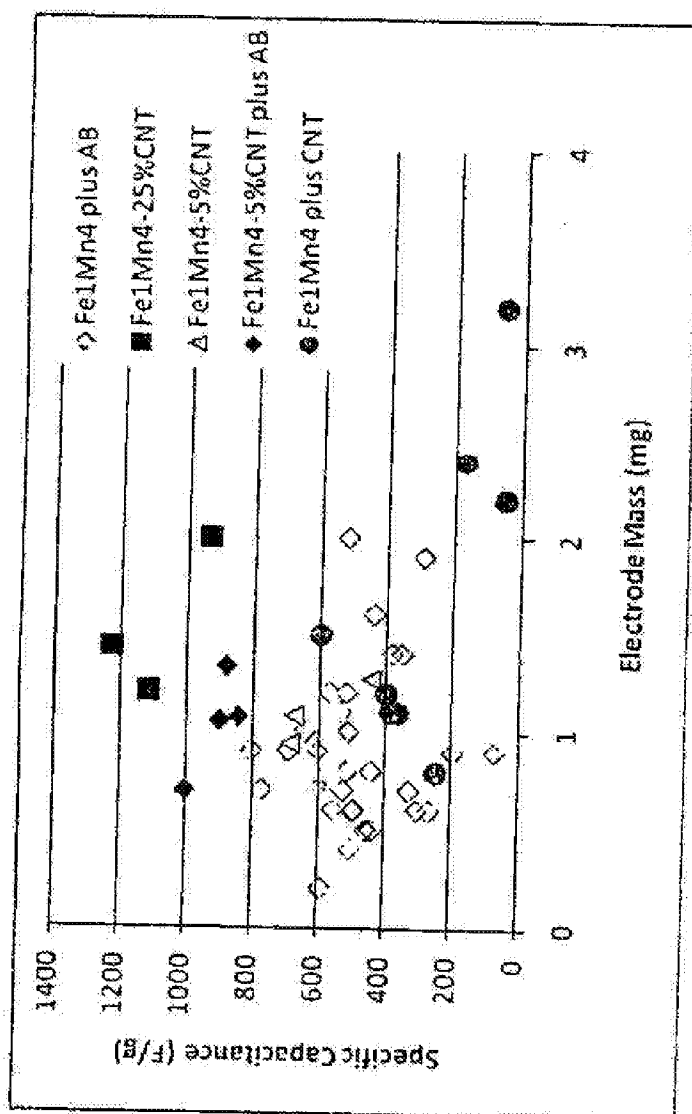


Fig. 15

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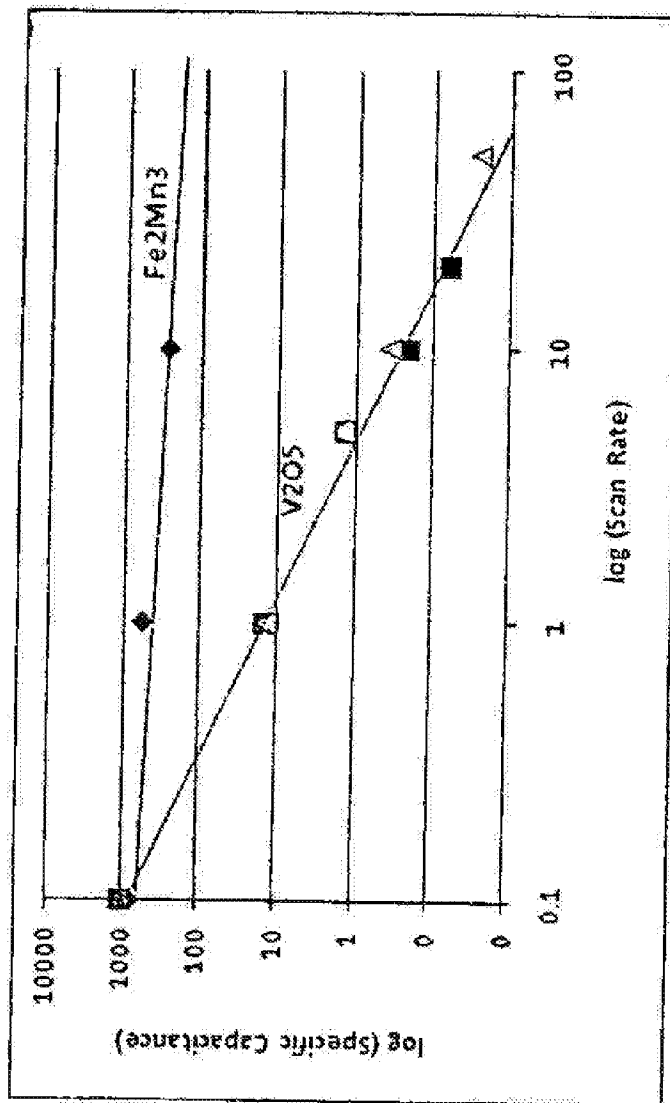


Fig. 16

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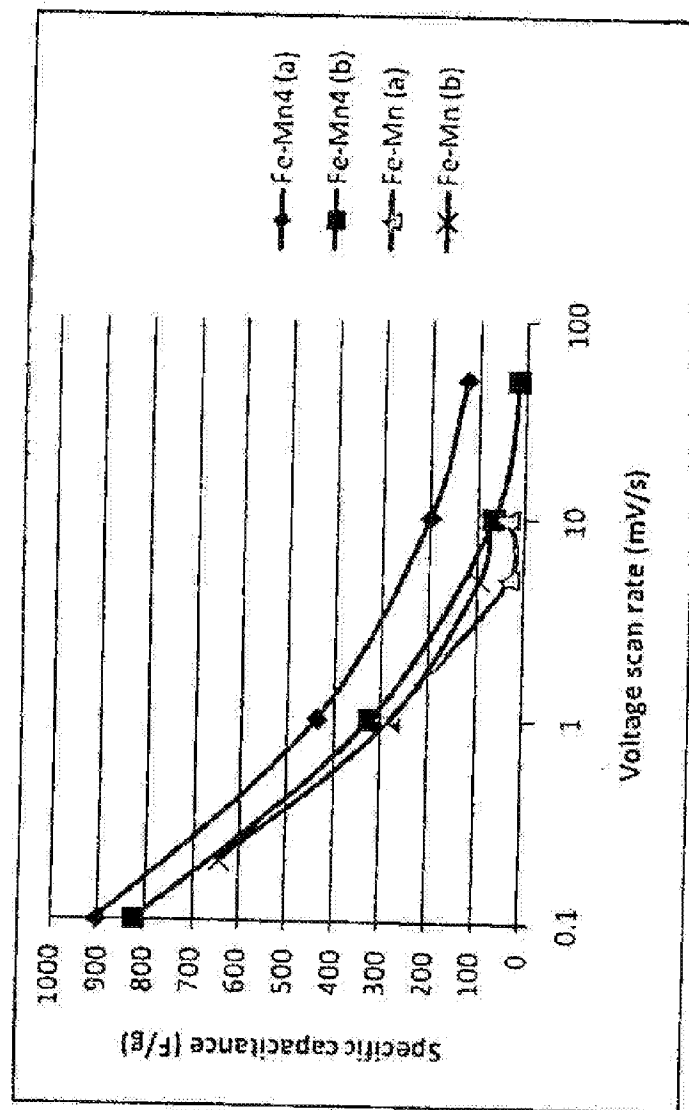


Fig. 17

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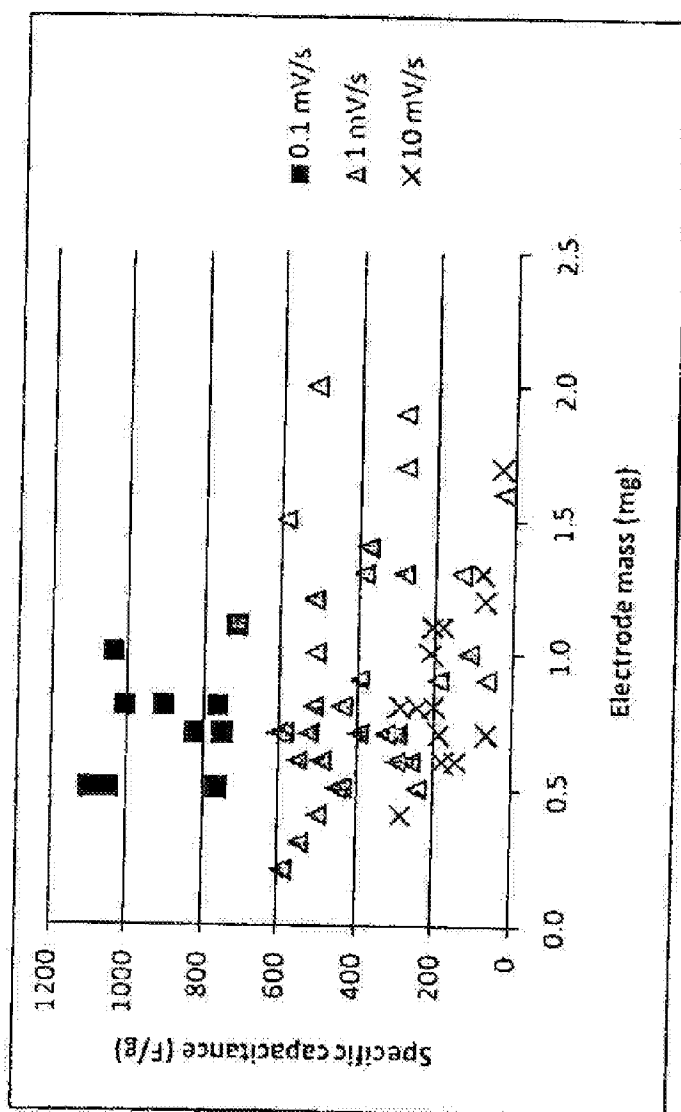


Fig. 18

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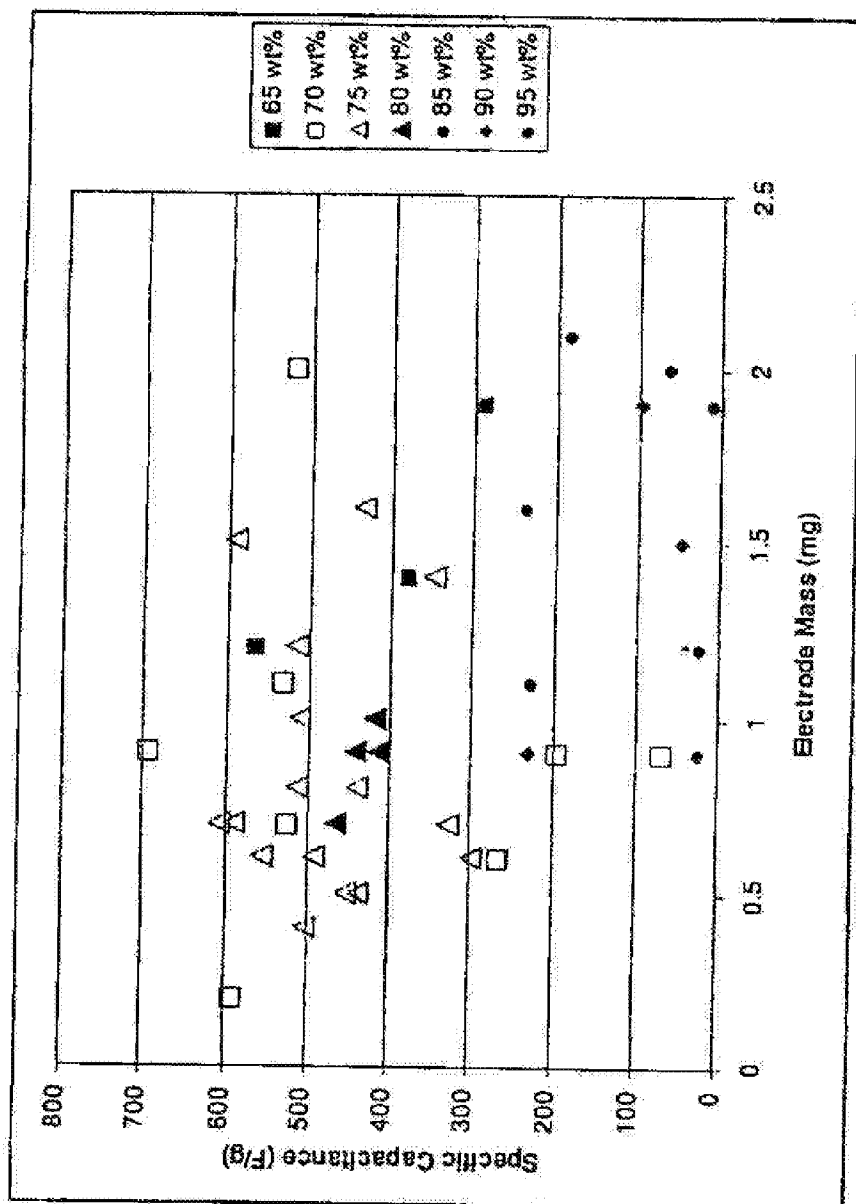


Fig. 19

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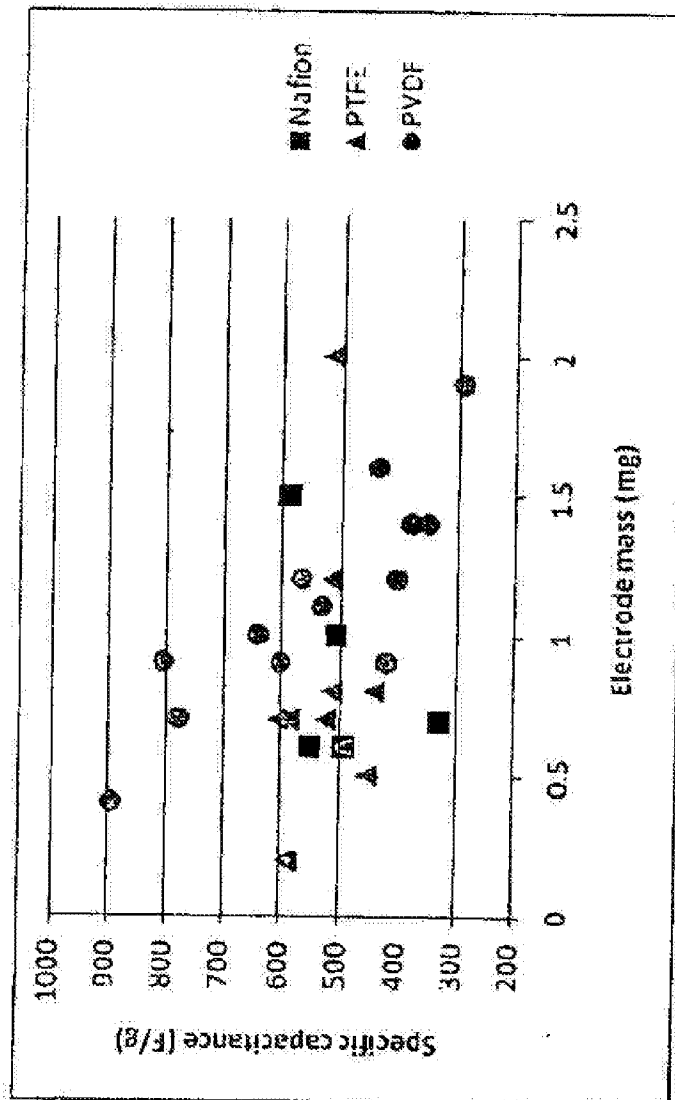


Fig. 20

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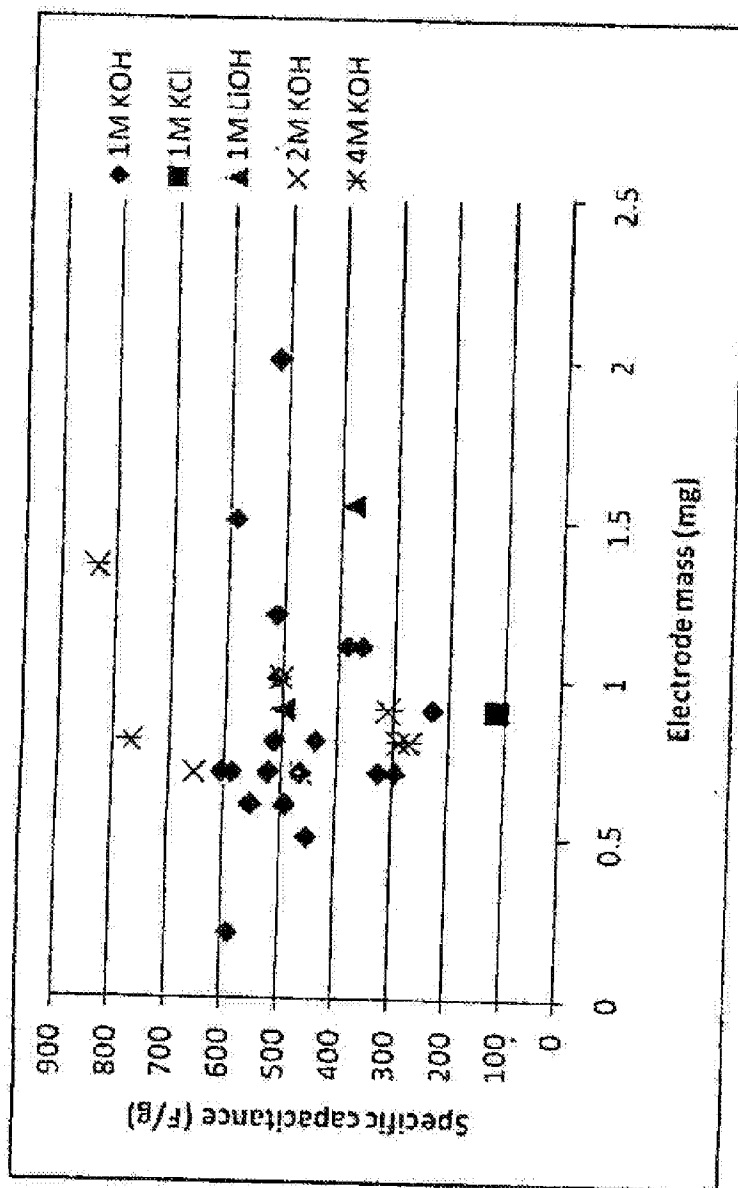


Fig. 21

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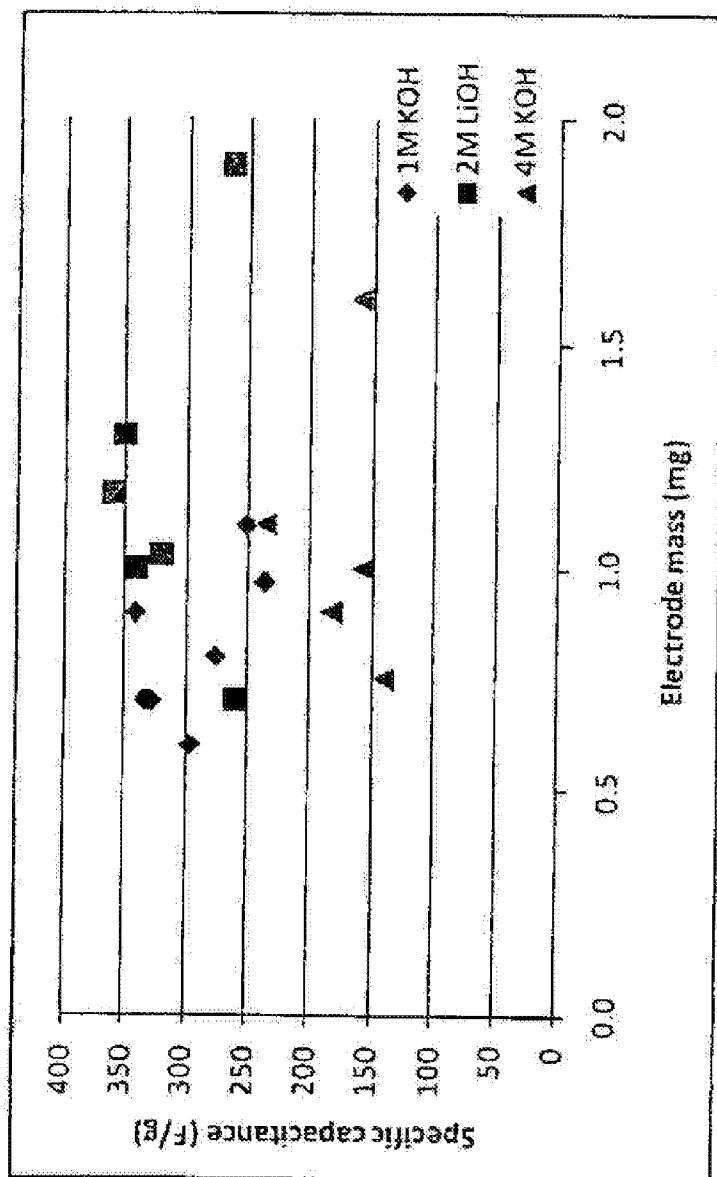


Fig. 22

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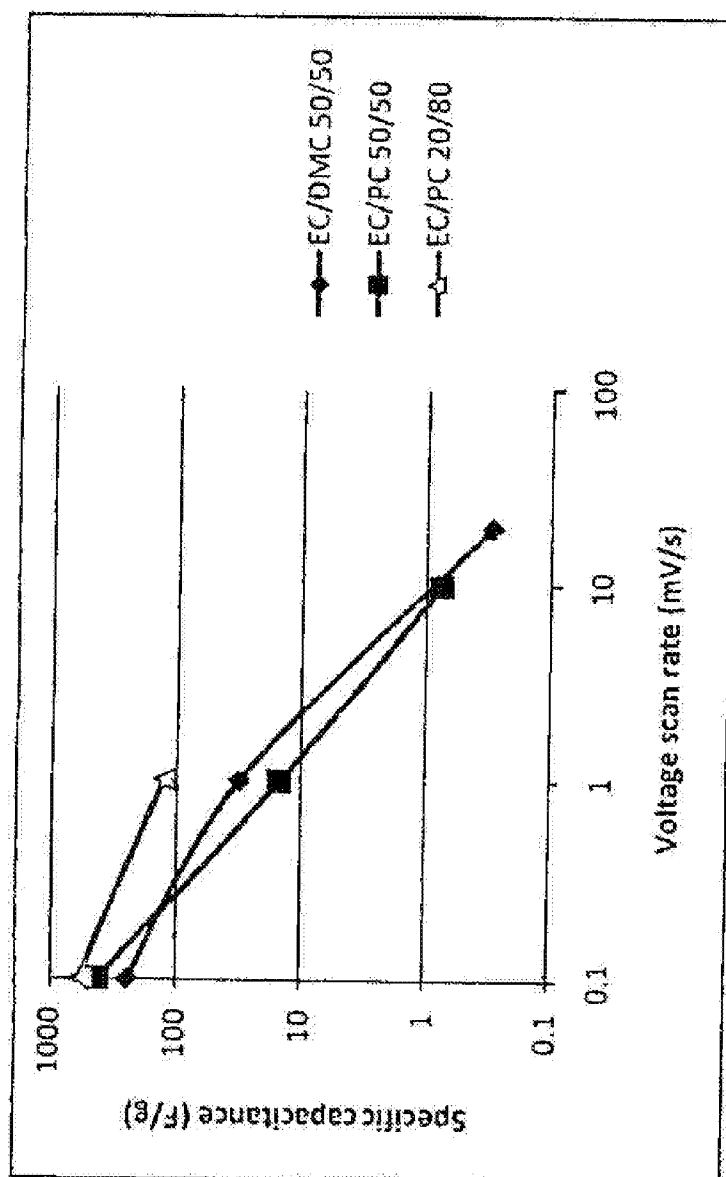


Fig. 23

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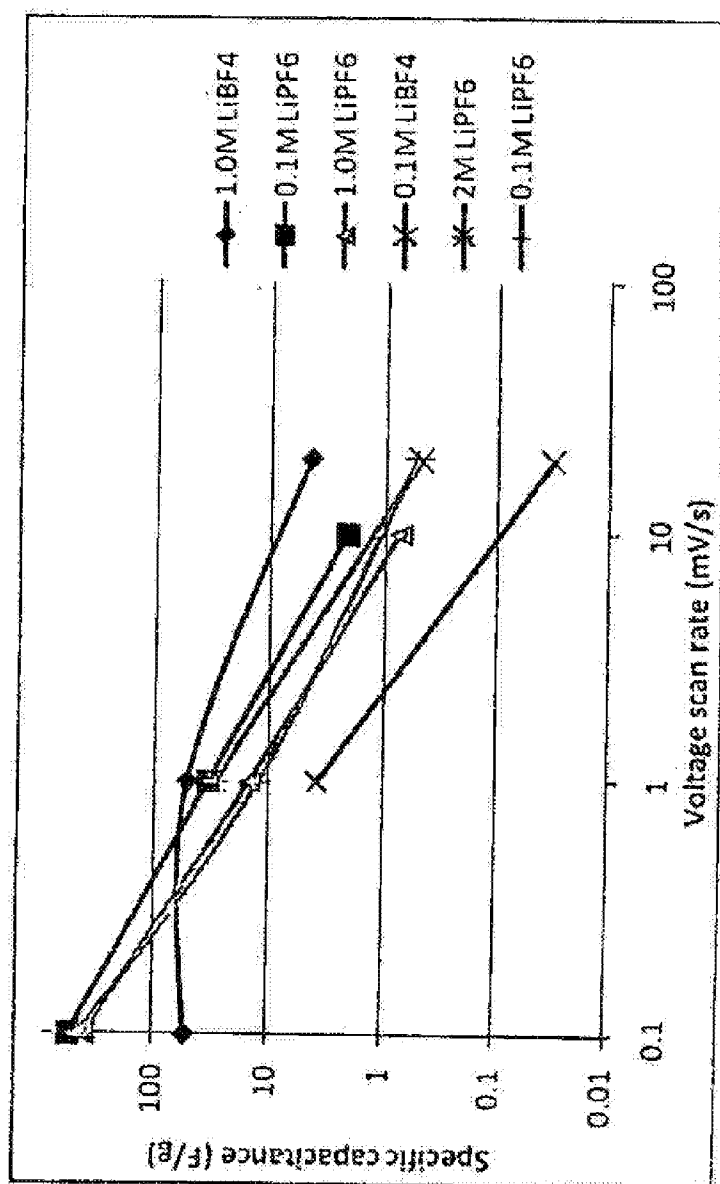


Fig. 24

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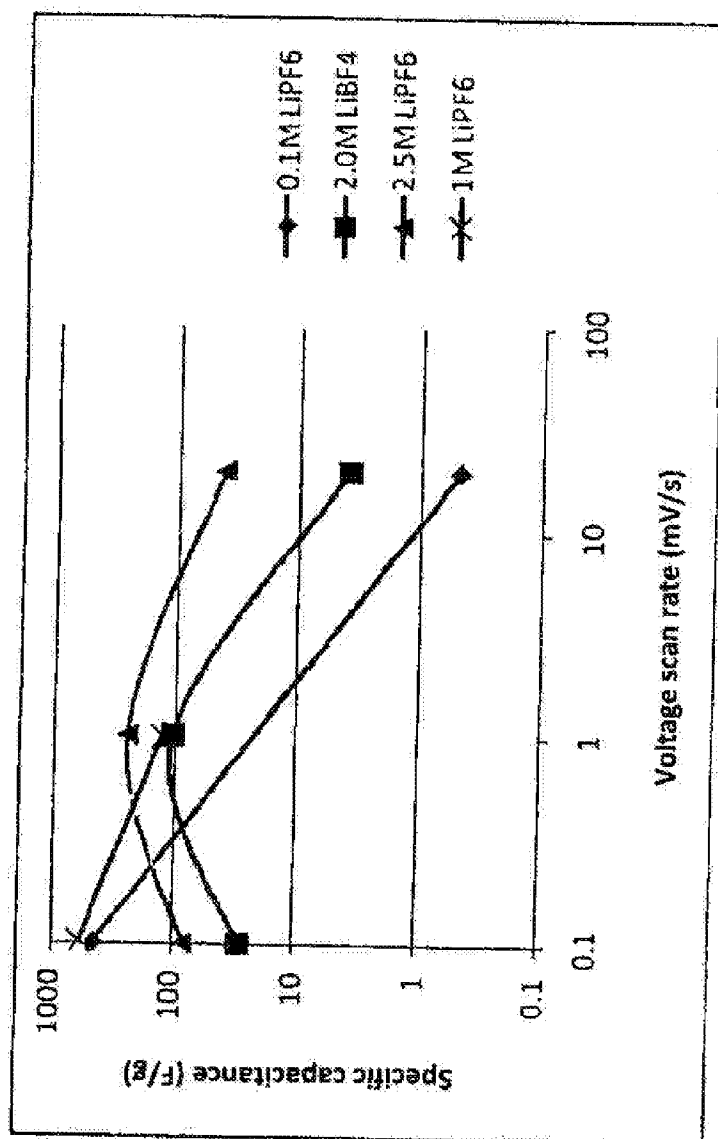


Fig. 25

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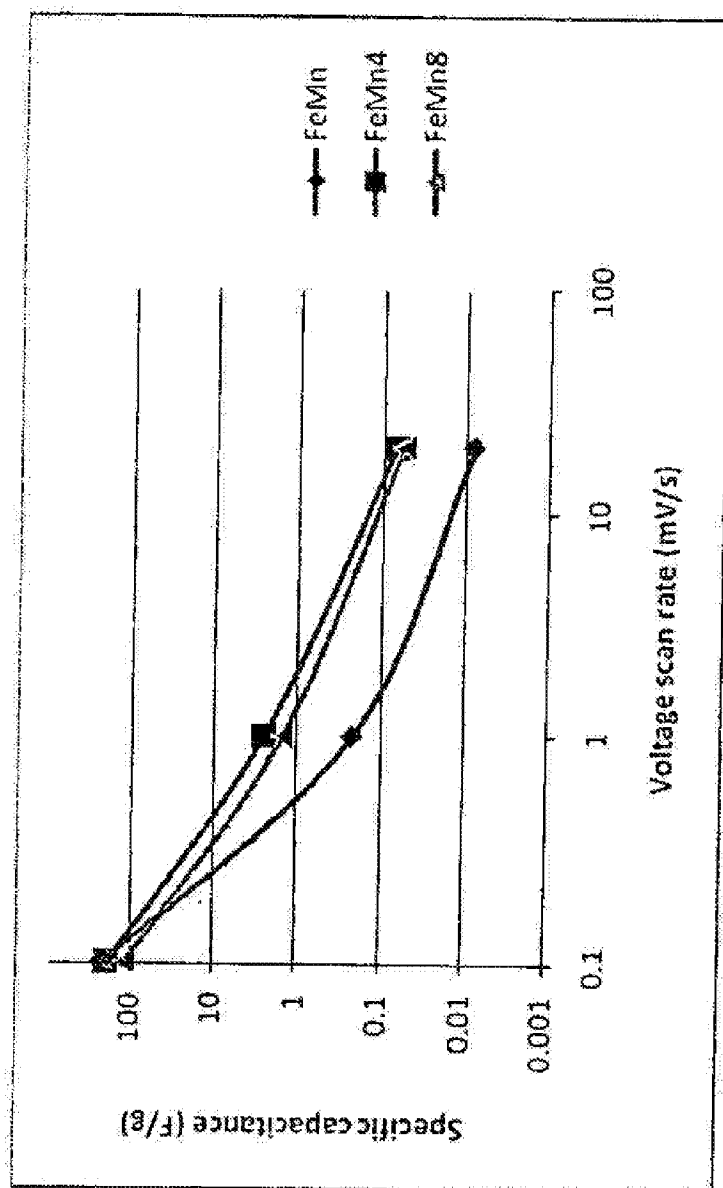


Fig. 26

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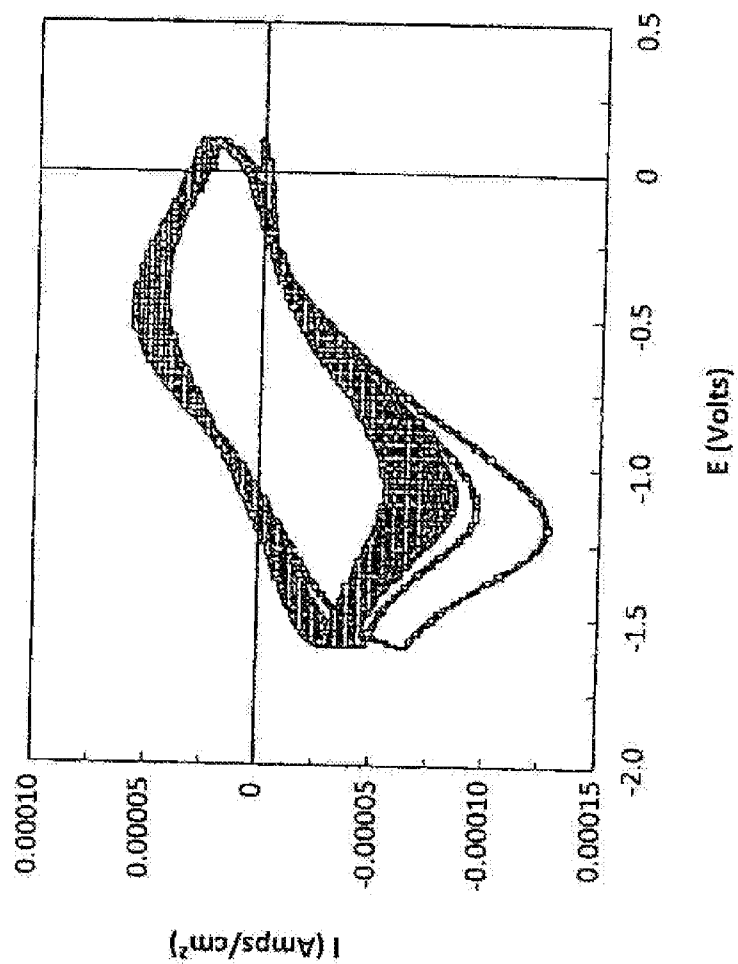


Fig. 27

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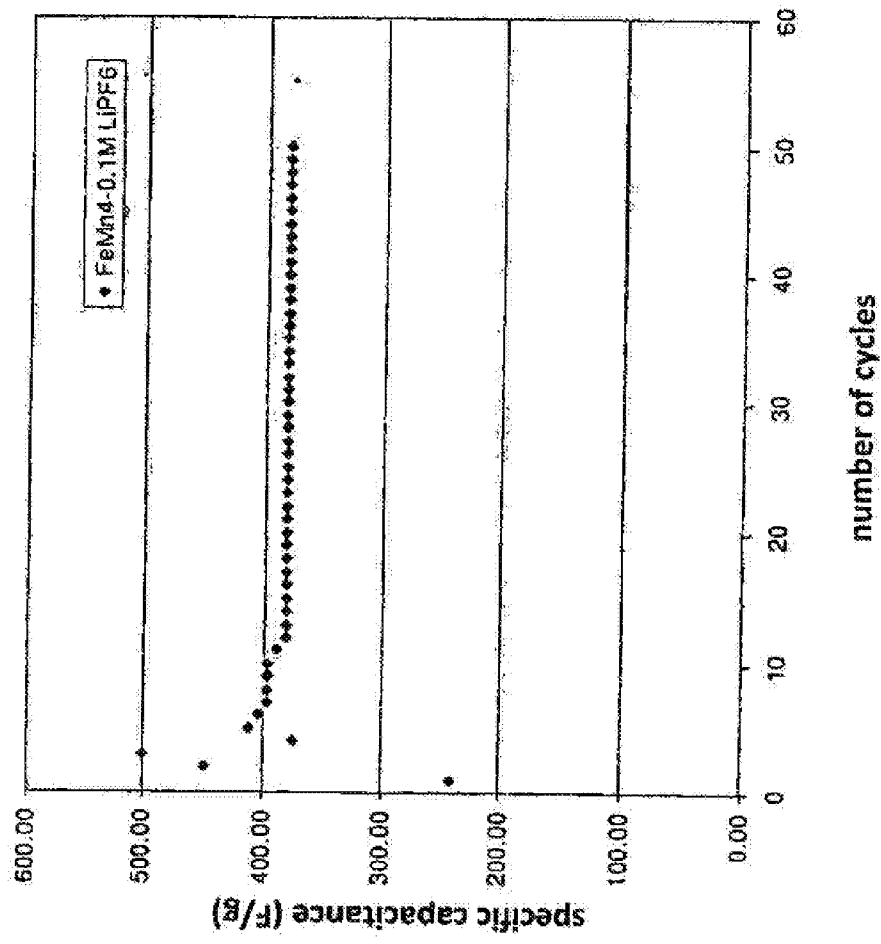


Fig. 28

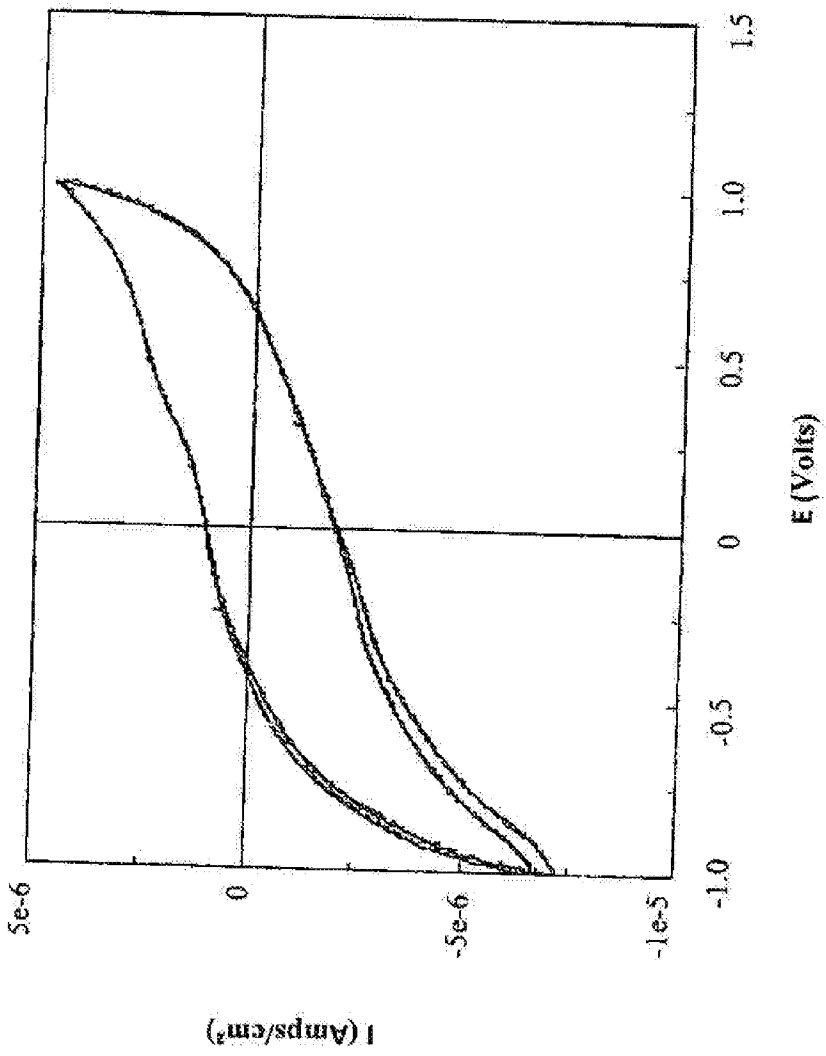


Fig. 29

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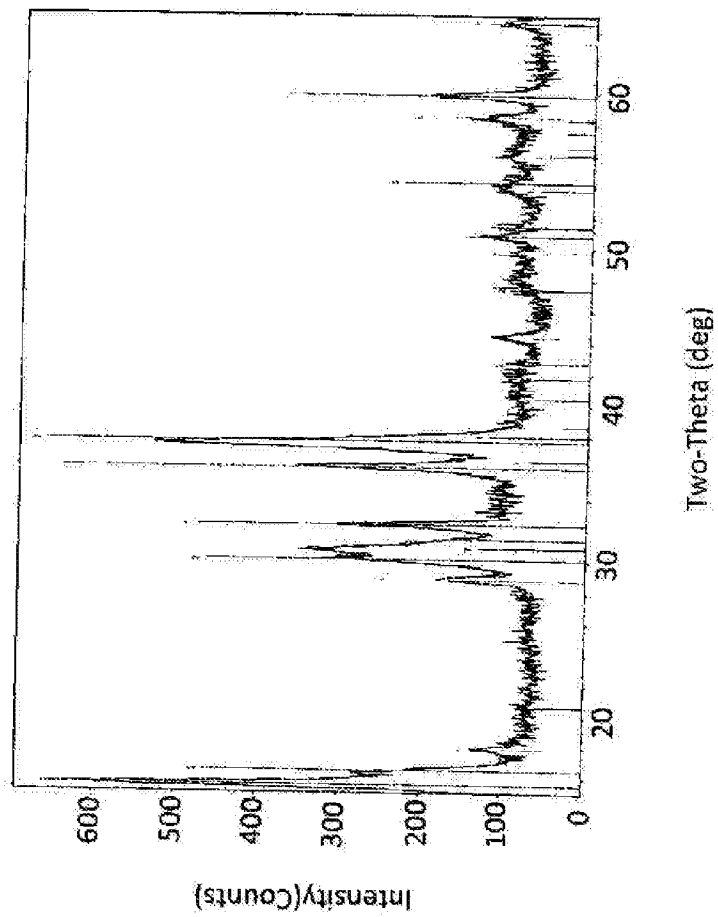


Fig. 30

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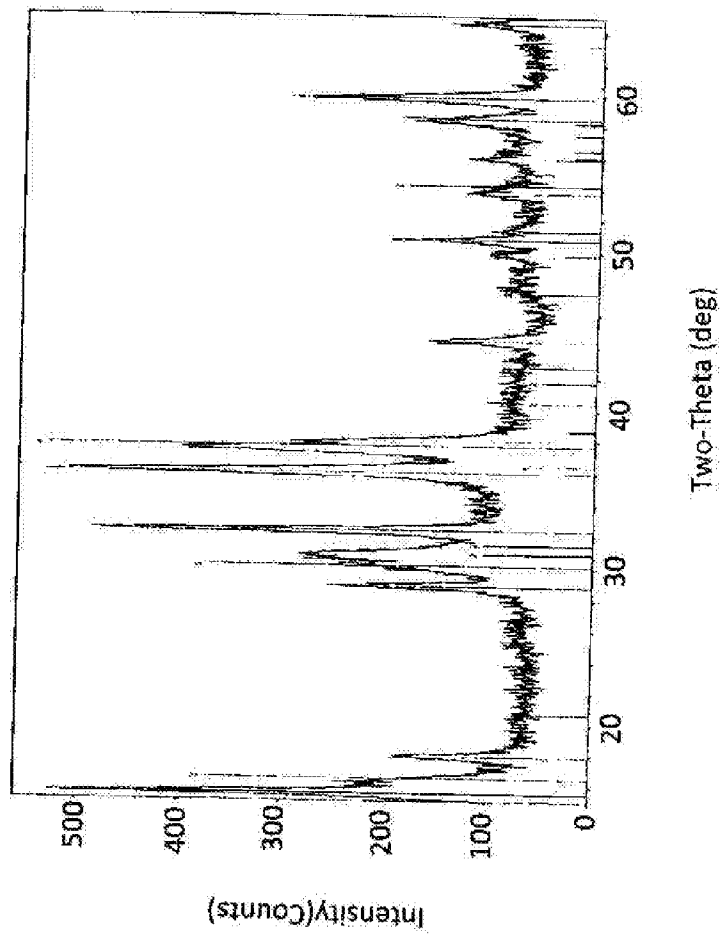


Fig. 31

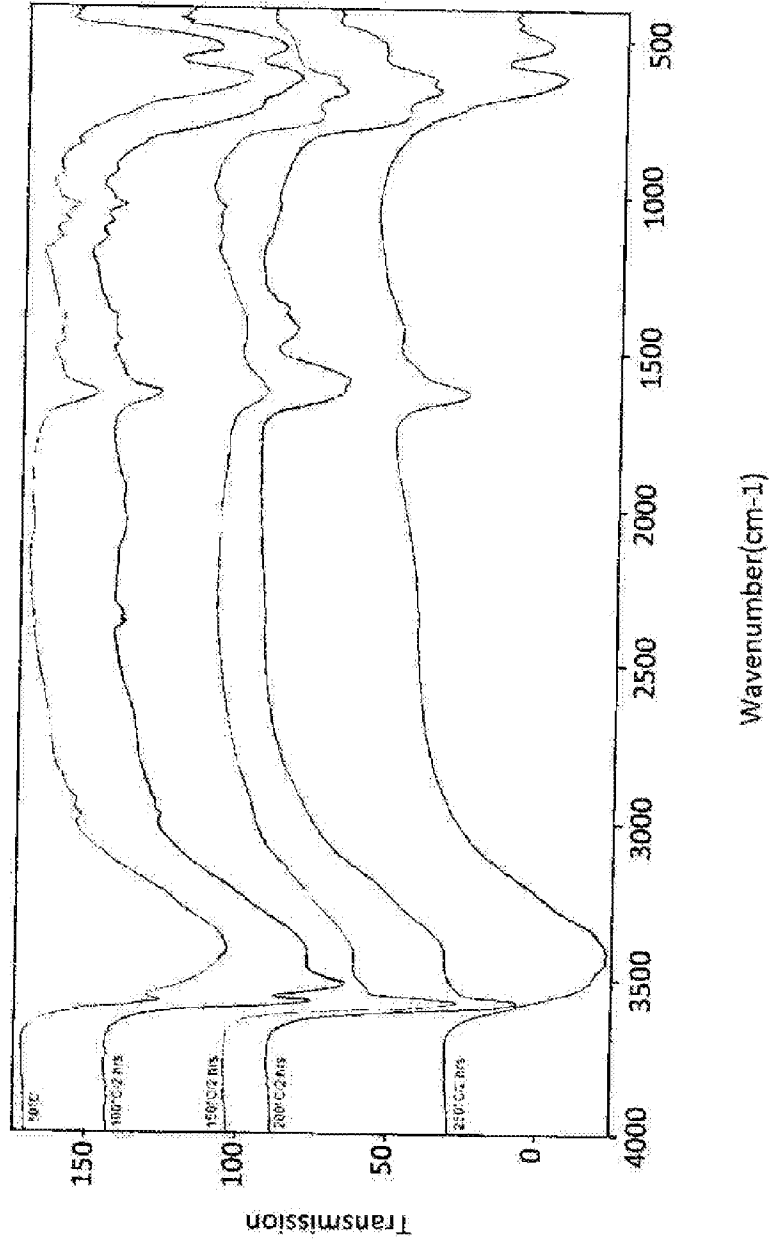


Fig. 32

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/029515

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01G9/058 H01G9/155

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SHIN-LIANG KUO, NAE-LIH WU: "Electrochemical Capacitor of MnFe ₂ O ₄ with NaCl Electrolyte" ELECTROCHEMICAL AND SOLID-STATE LETTERS, vol. 8, no. 10, 4 August 2005 (2005-08-04), pages A495-A499, XP002586556 Abstract and Experimental	1-12, 15-22, 30
A	Johann Gottlob Krüger: "Geschichte der Erde in den allerältesten Zeiten" 1746, Lüderwaldische Buchhandlung, Halle (Germany), XP002586557 pages 175-184, ----- -/--	30

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

14 June 2010

Date of mailing of the international search report

31/08/2010

Name and mailing address of the ISA/
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Authorized officer

Plützer, Stefan

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/029515

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Johann Beckmann: "Beyträge zur Geschichte der Erfindungen" 1786, Paul Gotthelf Kummer , Leipzig (Germany) , XP002586558 vol. 4, pages 571-575, -----	30
A	JP 2007 181278 A (MORIOKA SEIKO INSTRUMENTS INC) 12 July 2007 (2007-07-12) abstract; figure 2 -----	18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/029515

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-12, 19-22(completely); 15-18, 30(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-12, 19-22(completely); 15-18, 30(partially)

A capacitor comprising an electrode whereby the electrode comprises a metaloxide comprising Mn and Fe in a molar ratio Mn/Fe of 3:1 to 5:1; and a method of making the same

2. claims: 13, 14(completely); 15-18, 30(partially)

A capacitor comprising an electrode whereby the electrode comprises a metal oxide comprising Ni, Co and Fe, whereby the molar ratio Ni/Co is in the range of 0.5 to 2 and the molar ratio Ni/Fe is in the range of 1.0 to 10.

3. claims: 23-29(completely); 30(partially)

A capacitor and a method of producing the same. The capacitor comprises two electrodes, an electrolyte between the electrode whereby the electrolyte comprises a Li salt in a carbonate solution, whereby the carbonate solution comprises 10-30% ethylene carbonate and 70-90% propylene carbonate.

4. claim: 31

A method of making a capacitor comprising the steps of providing a carbon electrode in a first Li-containing solution, intercalating Li into the electrode to form a Li-intercalated electrode, removing the electrode from the first Li-containing solution and placing the Li-intercalated electrode into a second Li-containing solution.

5. claims: 32-35

A method of making an electrode comprising the steps of forming a solution comprising carbon particles and a dissolved metal compound, reacting the metal compound to form a gel, converting the gel into metal oxide nanoparticles, combining the metal oxide nanoparticles with a binder, compacting the metal oxide particles and binder into an electrode.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/029515

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2007181278 A	12-07-2007	NONE	